

FORM PTO-1390  
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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

0020-4951P

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

**10/048021**

INTERNATIONAL APPLICATION NO.

PCT/JP00/05229

INTERNATIONAL FILING DATE

August 4, 2000

PRIORITY DATE CLAIMED

August 5, 1999

**TITLE OF INVENTION**

SUPPORTED RUTHENIUM OXIDE CATALYST, PROCESS FOR PREPARING SUPPORTED RUTHENIUM CATALYST AND  
PROCESS FOR PRODUCING CHLORINE

**APPLICANT(S) FOR DO/EO/US**

HIBI, Takuo; OKUHARA, Toshio; SEKI, Kohei; ABEKAWA, Hiroaki; HAMAMATSU, Hiroshi

**Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:**

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau. WO 01/10550
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☒ is transmitted herewith.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4)
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

**Items 11. to 20. below concern document(s) or information included:**

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98, Form PTO-1449(s), and International Search Report (PCT/ISA/210) with 0 cited document(s).
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:
  - 1.) PCT/IPEA/409 and PCT/IPEA/416
  - 2.) PCT/IB/304 and PCT/IB/308
  - 3.) Zero (0) sheets of Formal Drawings

**JG13 Rec'd PCT/PTO 28 JAN 2002**

U.S. APPLICATION NO (if known, see 37 CFR 1.5) <div style="font-size: 1.5em; font-weight: bold;">107048021</div>		INTERNATIONAL APPLICATION NO PCT/JP00/05229		ATTORNEY'S DOCKET NUMBER 0020-4951P	
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21. <input checked="" type="checkbox"/> The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. .... <b>\$1,040.00</b>  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... <b>\$890.00</b>  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO. .... <b>\$740.00</b>  International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... <b>\$710.00</b>  International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4). .... <b>\$100.00</b> <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>CALCULATIONS      PTO USE ONLY</b>	
				\$	890.00
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	130.00
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	12 - 20 =	0	X \$18.00	\$	0
Independent Claims	3 - 3 =	0	X \$84.00	\$	0
MULTIPLE DEPENDENT CLAIM(S) (if applicable)      None      + \$280.00				\$	0
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$	1020.00
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	0
<b>SUBTOTAL =</b>				\$	1020.00
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	0
<b>TOTAL NATIONAL FEE =</b>				\$	1020.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). <b>\$40.00</b> per property +				\$	0
<b>TOTAL FEES ENCLOSED =</b>				\$	1020.00
				Amount to be: refunded	\$
				charged	\$

a. ☒ A check in the amount of \$ **1020.00** to cover the above fees is enclosed.

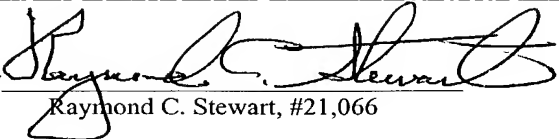
b. ☐ Please charge my Deposit Account. No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees.  
 A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any  
 overpayment to Deposit Account No. 02-2448.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR  
 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

Send all correspondence to:  
**Birch, Stewart, Kolasch & Birch, LLP** or Customer No. 2292  
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**Date:** January 28, 2002

By   
 Raymond C. Stewart, #21,066

10048021 107048021

JG12 Rec'd PCT/PTO 28 JAN 2002

PATENT  
0020-4951P

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant: HIBI, Takuo et al.  
Int'l. Appl. No.: PCT/JP00/05229  
Appl. No.: New Group:  
Filed: January 28, 2002 Examiner:  
For: SUPPORTED RUTHENIUM OXIDE CATALYST,  
PROCESS FOR PREPARING SUPPORTED  
RUTHENIUM CATALYST AND PROCESS FOR  
PRODUCING CHLORINE

PRELIMINARY AMENDMENT

**BOX PATENT APPLICATION**

Assistant Commissioner for Patents  
Washington, DC 20231

January 28, 2002

Sir:

The following Preliminary Amendments and Remarks are respectfully submitted in connection with the above-identified application.

AMENDMENTS

IN THE SPECIFICATION:

Please amend the specification as follows:

Before line 1, insert --This application is the national phase under 35 U.S.C. § 371 of PCT International Application No. PCT/JP00/05229 which has an International filing date of August 4, 2000, which designated the United States of America.--

Docket No. 0020-4951P

REMARKS

The specification has been amended to provide a cross-reference to the previously filed International Application.


Entry of the above amendments is earnestly solicited. An early and favorable first action on the merits is earnestly solicited.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By

  
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(Rev. 11/13/01)



10/048021  
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## DESCRIPTION

SUPPORTED RUTHENIUM OXIDE CATALYST, PROCESS FOR PREPARING  
SUPPORTED RUTHENIUM CATALYST AND PROCESS FOR PRODUCING  
CHLORINE

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## FIELD OF THE INVENTION

The present invention relates to a supported ruthenium oxide catalyst, a process for preparing a supported ruthenium oxide catalyst or a supported ruthenium chloride catalyst, and process for producing chlorine. More particularly, the present invention relates to a supported ruthenium oxide catalyst which has a high catalytic activity and thus produces purpose substance in a smaller amount at a lower temperature, and which is less sintered during the reaction, simplifies the production steps, and suffers less deactivation, a process for preparing a supported ruthenium oxide catalyst or a supported ruthenium chloride catalyst which have the same characteristics as above, and a process for producing chlorine by oxidizing hydrogen chloride with oxygen in the presence of such a catalyst.

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## PRIOR ART

Firstly, a supported ruthenium oxide catalyst is explained. The supported ruthenium oxide catalyst is useful as a catalyst for the production of chlorine by the

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oxidation of hydrogen chloride, and it is known that the ruthenium oxide catalyst can be prepared by hydrolyzing ruthenium chloride, oxidizing the hydrolyzed product and then calcining the oxidized product. For example, US

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Patent No. 5,871,707 describes that a ruthenium oxide catalyst supported on titanium oxide is prepared by hydrolyzing a ruthenium compound with an alkali metal hydroxide, supporting the hydrolyzed product on titanium hydroxide, and calcining the supported product under air.

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The present inventors have found that a supported ruthenium oxide catalyst can be obtained by oxidizing a supported metal ruthenium catalyst (JP-A-10-338502). The supported metal ruthenium catalyst may be prepared by supporting ruthenium chloride on a carrier, drying the supported

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ruthenium chloride and heating it in a hydrogen stream. However, when ruthenium chloride is reduced with hydrogen, ruthenium is sintered, and thus the supported ruthenium oxide catalyst, which is produced by oxidizing the catalyst reduced with hydrogen, has a low activity. That is a

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problem.

Hitherto, a supported ruthenium oxide catalyst comprising titanium oxide as a carrier is known. However, from the viewpoint of a catalyst life, the development of a supported ruthenium oxide catalyst, the catalyst life of which is prolonged by the improvement of the carrier, has

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been sought.

Conventionally, a catalyst having a high catalytic activity can be prepared by treating a ruthenium compound, in particular, a ruthenium halide, supported on a carrier with an alkaline solution of hydrazine, but the development of a ruthenium base catalyst having a higher catalyst activity through the improvement of a preparation method has been desired. Furthermore, it is desired to develop a ruthenium oxide catalyst having a higher catalytic activity by increasing a proportion of a ruthenium oxide surface which is effective for the reaction in the ruthenium oxide particles supported on a carrier.

Next, a method for preparing a supported ruthenium oxide catalyst or a supported ruthenium chloride catalyst is explained. Such a method has the same problems as those described in the above in connection with the supported ruthenium oxide catalyst. In addition to such problems, there is a problem that ruthenium oxide or a ruthenium halide supported on a carrier is sintered during a reaction and thus the catalytic activity deteriorates. Therefore, it is desired to provide a catalyst which less suffers from the sintering of ruthenium oxide or the ruthenium halide supported on the carrier during the reaction. Besides, the decrease of the steps of a process for preparing a catalyst is more preferable, and it is desired to prepare a catalyst

having a high catalytic activity by a simple process. In  
 general, there is a problem that the activity of the  
 catalyst decreases during the reaction. Accordingly, the  
 development of a catalyst which less suffers from the  
 5 decrease of the catalytic activity.

Now, a method for producing chlorine is explained.

It is well known that chlorine is useful as a raw  
 material of vinyl chloride, phosgene, etc. and can be  
 produced by oxidizing hydrogen chloride. For example, the  
 10 Deacon reaction using a Cu catalyst is well known. For  
 instance, GB Patent No. 1,046,313 discloses a process for  
 producing chlorine comprising oxidizing hydrogen chloride  
 in the presence of a catalyst containing a ruthenium  
 compound, and describes that ruthenium (III) chloride is  
 15 particularly effective among the ruthenium compounds.  
 Furthermore, this GB Patent discloses the use of a  
 ruthenium compound supported on a carrier, and exemplifies  
 silica gel, alumina, pumice and ceramic materials as  
 carriers. In the Examples, a ruthenium chloride catalyst  
 20 supported on silica was used. However, when an experiment  
 was carried out using a catalyst which was prepared by  
 repeating the process for preparing (or tracing) a  
 ruthenium (III) chloride catalyst supported on silica,  
 which is disclosed in this GB Patent, the ruthenium  
 25 compound as the catalyst component remarkably volatilized,

and therefore it was disadvantageous for industrial use.  
 EP 0 184 414 A2 discloses a process for producing chlorine  
 by oxidizing hydrogen chloride in the presence of a  
 chromium oxide catalyst. However, conventionally known  
 5 processes have a problem that the activity of the catalyst  
 is insufficient, and a high reaction temperature is  
 required.

When the activity of the catalyst is lower, a higher  
 reaction temperature is required. However, since the  
 10 reaction of oxidizing hydrogen chloride with oxygen for the  
 production of chlorine is an equilibrium reaction, the  
 higher reaction temperature is disadvantageous from the  
 viewpoint of equilibrium, and decreases the equilibrium  
 conversion of hydrogen chloride. When the catalyst has a  
 15 high activity, the reaction temperature can be decreased  
 and, therefore, the reaction becomes advantageous from the  
 viewpoint of the equilibrium, and the higher conversion of  
 hydrogen chloride can be attained. When the reaction  
 temperature is high, the activity of the catalyst may be  
 20 decreased by the volatilization of the catalyst component.  
 From this point of view, it has been required to develop a  
 catalyst which can be used at a low temperature.

For the industrial use, a catalyst is required to have  
 both a high activity of the catalyst and a high activity  
 25 per the unit mass of ruthenium contained in the catalyst.

One object of the present invention is to provide a supported ruthenium oxide catalyst which has a high catalytic activity and thus produces a desired substance in

a smaller amount at a lower temperature, and which is less sintered during the reaction, simplifies the production steps, and suffers less deactivation.

Another object of the present invention is to provide  
5 a process for preparing a supported ruthenium oxide catalyst or a supported ruthenium chloride catalyst which has the same characteristics as those described above.

A further object of the present invention is to provide a process for producing chlorine by oxidizing  
10 hydrogen chloride with oxygen in the presence of such a supported ruthenium oxide catalyst.

According to the first aspect of the present invention, there is provided a supported ruthenium oxide catalyst selected from the group consisting of:

15 (1) a supported ruthenium oxide catalyst comprising titanium oxide which contains the rutile crystal form, and which is obtained by calcination at a temperature of at least 550°C, as a carrier;

(2) a supported ruthenium oxide catalyst having a  
20 carbon monoxide adsorption amount of at least 87.5 ml per one gram of ruthenium contained in the catalyst, which is measured by the following steps of:

reducing 0.1 g of said catalyst at 220°C for 60  
minutes with flowing a hydrogen gas at a flow rate of 50  
25 ml/min. under atmospheric pressure, and

calcining said supported one in an atmosphere selected  
25 from the group consisting of an oxidizing gas atmosphere,



an inert gas atmosphere and a reducing gas atmosphere;

(2) a process comprising the steps of:

supporting a ruthenium compound on a carrier,

calcining said supported one at a temperature of at

5 least 200°C in an atmosphere selected from the group  
consisting of an oxidizing gas atmosphere, an inert gas  
atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of  
hydrazine and an alkaline compound,

10 and

oxidizing said hydrazine-treated one

wherein said supported ruthenium oxide catalyst has a  
carbon monoxide adsorption amount of at least 87.5 ml per  
one gram of ruthenium contained in the catalyst, which is

15 measured by the following steps of:

reducing 0.1 g of said catalyst at 220°C for 60  
minutes with flowing a hydrogen gas at a flow rate of 50  
ml/min. under atmospheric pressure, and

conducting a metal surface area measuring method

20 according to a carbon monoxide pulse;

(3) a process comprising the steps of:

supporting a ruthenium compound on a carrier,

calcining said supported one at a temperature of at

least 200°C in an atmosphere selected from the group

25 consisting of an oxidizing gas atmosphere, an inert gas

atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of hydrazine and an alkaline compound,

and

5 oxidizing said hydrazine-treated one;

(4) a process comprising the steps of:

supporting a ruthenium compound on a carrier,

and

10 calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, wherein, when the peak intensity ratio of the produced catalyst and that of the catalyst after a 50 hours reaction test, which are measured by an extended X-ray absorption  
15 fine structure analysis (EXAFS) method, are A(b) and B(b) respectively, the peak intensity ratios A(b) and B(b) satisfy the following equation (1):

$$1 \leq B(b)/A(b) \leq 1.45 \quad (1)$$

provided that  $A(b) \leq 0.8$ ,

20 wherein A(b) is a peak intensity ratio of as-produced Catalyst b measured by the EXAFS method, and B(b) is a peak intensity ratio of Catalyst b measured by the EXAFS method after the 50 hours reaction test;

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in which

25 the 50 hours reaction test is carried out by filling

supported ruthenium oxide Catalysts a and b in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and supplying, under atmospheric pressure, a hydrogen chloride gas at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at  $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , wherein Catalyst a is a catalyst having a chlorine formation activity per unit mass of catalyst of  $2 \times 10^{-4}$  to  $3 \times 10^{-4}$  mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at  $300^{\circ}\text{C}$  with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide Catalyst produced by the above process, and in which

EXAFS method: Catalyst b is measured by an X-ray absorption fine structure analysis (XAFS) method at the Ru-K absorption edge, and the peak intensity of the catalyst is evaluated by the peak around 0.32 nm in a radial distribution function obtained by the Fourier transformation of the EXAFS spectrum, wherein the peak intensity corresponds to the number of the second nearest neighbor ruthenium atoms of the X-ray absorbing ruthenium atoms in ruthenium dioxide, and the peak intensity ratio of

the catalyst is calculated by dividing the peak intensity of the catalyst by that of ruthenium oxide having a particle size of at least 10 nm;

(5) a process comprising the following steps but not a treating step with hydrazine:

supporting a ruthenium compound on a titanium oxide carrier containing the rutile crystal form, and

calcining said supported one at a temperature of 200°C to 600°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere; and

(6) a process comprising the following steps but neither a calcining step nor a treating step with hydrazine:

supporting a ruthenium halide on a titanium oxide carrier containing the rutile crystal form, and

drying said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere at a temperature of 20°C to less than 200°C.

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According to the third aspect of the present invention, there is provided a process for producing chlorine by

oxidizing hydrogen chloride with oxygen, which uses at least one catalyst selected from the group consisting of the following catalysts (1) to (6):

(1) a supported ruthenium oxide catalyst comprising  
5 titanium oxide which contains the rutile crystal form, and which is obtained by calcination at a temperature of at least 550°C, as a carrier;

(2) a supported ruthenium oxide catalyst having a carbon monoxide adsorption amount of at least 87.5 ml per  
10 one gram of ruthenium contained in the catalyst, which is measured by the following steps of:

reducing 0.1 g of said catalyst at 220°C for 60 minutes with flowing a hydrogen gas at a flow rate of 50 ml/min. under atmospheric pressure, and

15 conducting a metal surface area measuring method according to a carbon monoxide pulse;

(3) a supported ruthenium oxide catalyst obtained by a preparation process comprising the steps of:

supporting a ruthenium compound on a carrier,

20 calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

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treating said calcined one with a mixed solution of  
25 hydrazine and an alkaline compound,

and

oxidizing said hydrazine-treated one;

(4) a supported ruthenium oxide catalyst produced by a process comprising the steps of:

5 supporting a ruthenium compound on a carrier,

and

calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

10 wherein, when the peak intensity ratio of the produced catalyst and that of the catalyst after a 50 hours reaction test, which are measured by an extended X-ray absorption fine structure analysis (EXAFS) method, are A(b) and B(b) respectively, the peak intensity ratios A(b) and B(b) satisfy the following equation (1):

$$1 \leq B(b)/A(b) \leq 1.45 \quad (1)$$

provided that  $A(b) \leq 0.8$ ,

wherein A(b) is a peak intensity ratio of as-produced Catalyst b measured by the EXAFS method, and B(b) is a peak  
20 intensity ratio of Catalyst b measured by the EXAFS method after the 50 hours reaction test;

in which

50 Hours reaction test: Supported ruthenium oxide

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Catalysts a and b are filled in a reactor in this order

25 from the inlet of the reactor in a weight ratio of 1:10

(Catalyst a to Catalyst b), and a hydrogen chloride gas is supplied under atmospheric pressure at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at  $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , in which Catalyst a is a supported ruthenium oxide catalyst having a chlorine formation activity per unit mass of the catalyst of  $2 \times 10^{-4}$  to  $3 \times 10^{-4}$  mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at  $300^{\circ}\text{C}$  with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide catalyst produced by the above process, and in which

EXAFS method: Catalyst b is measured by an X-ray absorption fine structure analysis (XAFS) method at the Ru-K absorption edge, and the peak intensity of the catalyst is evaluated by the peak around 0.32 nm in a radial distribution function obtained by the Fourier transformation of the EXAFS spectrum, wherein the peak intensity corresponds to the number of the second nearest neighbor ruthenium atoms of the X-ray absorbing ruthenium atoms in ruthenium dioxide, and the peak intensity ratio of the catalyst is calculated by dividing the peak intensity of the catalyst by that of ruthenium oxide having a

particle size of at least 10 nm;

(5) a supported ruthenium oxide catalyst produced by a process comprising the following steps but not a treating step with hydrazine:

5 supporting a ruthenium compound on a titanium oxide carrier containing the rutile form, and

calcining said supported one at a temperature of 200°C to 600°C in an atmosphere selected from the group

10 consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere; and

(6) a supported ruthenium oxide catalyst produced by a process comprising the following steps but neither a calcining step nor a treating step with hydrazine:

15 supporting a ruthenium halide on a titanium oxide carrier containing the rutile crystal form, and

drying said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, 20 an inert gas atmosphere and a reducing gas atmosphere at a temperature of 20°C to less than 200°C.

#### DETAILED DESCRIPTION OF THE INVENTION

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25 The relationship of the catalysts described in the first to third aspects of the present inventions is



The catalyst (3) of the third aspect of the present invention is prepared by the process comprising four steps, that is, the steps of supporting a ruthenium compound on a carrier, calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, treating said calcined one with a mixed solution of hydrazine and an alkaline compound, and oxidizing said hydrazine-treated one. However, a catalyst, which is prepared by a process comprising one or two steps of the above four steps, has also its own characteristics, as it is presented as the catalyst from (4) to (6) of the third aspect of the present invention.

As shown in the catalyst which is prepared by the process comprising two steps, that is, the steps of supporting a ruthenium compound on a carrier, calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, has its own characteristics, as it is presented as the catalyst (4), (5) of the third aspect of the present invention.

Furthermore, a catalyst, which is prepared by a process comprising the one step, has its own characteristics, as it is presented as the catalyst (6) of the third aspect of the present invention.

Hereinafter, the inventions of the first to third aspects will be explained.

The catalyst (1) of the first aspect of the present invention is a supported ruthenium oxide catalyst comprising titanium oxide which contains the rutile crystal form, and which is obtained by calcination at a temperature of at least 550°C, as a carrier.

The calcination temperature is preferably from 550 to 1,000°C, more preferably from 600 to 1,000°C, particularly preferably from 700 to 1,000°C, most preferably from 800 to 1,000°C.

When such a carrier is used, a catalyst which suffers

Here, a test method for a reaction to obtain chlorine by oxidizing hydrogen chloride is explained.

Now, the preparation example of the catalyst according to the present invention is explained.

The supported ruthenium oxide catalyst may be prepared  
25 by treating a ruthenium compound supported on a carrier

with a reducing compound or a mixture of a reducing compound and a base compound, and oxidizing the treated ruthenium compound supported on the carrier.

Typically, titanium oxide containing rutile  
5 crystalline titanium oxide is used as a carrier.

In general, titanium oxide includes rutile crystalline titanium oxide, anatase crystalline titanium oxide, non-crystalline titanium oxide, etc.

Titanium oxide containing rutile crystal form used in  
10 the present invention means titanium oxide containing the rutile crystal, when the ratio of the rutile crystal to the anatase crystal in titanium oxide is measured by the X-ray diffraction analysis. This analysis will be explained in detail below.

15 When the chemical composition of the carrier used in the present invention consists of titanium oxide, the proportion of the rutile crystal can be determined from the ratio of the rutile crystal and the anatase crystal in titanium oxide measured by the X-ray diffraction analysis.  
20 However, since the carrier may contain a mixed oxide of titanium oxide and other metal oxide, in such a case, the content of the rutile crystal can be determined as described below.

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25 The oxide to be mixed with the titanium oxide include oxide of elements, and preferred examples of oxides include

alumina, zirconium oxide, silica, etc. The proportion of the rutile crystal in the mixed oxide is also determined from the ratio of the rutile crystal to the anatase crystal in titanium oxide measured by the X-ray diffraction analysis. In the present invention, titanium oxide should contain the rutile crystal. In this case, the content of the metal oxide other than titanium oxide is from 0 to 60 mass %. Preferably, the carrier does not contain any metal oxide other than titanium oxide.

Titanium oxide should contain the rutile crystal. The proportion of the rutile crystal is preferably at least 10 %, more preferably at least 30 %, in particular at least 80 %.

Various methods are known to prepare titanium oxide containing the rutile crystal. In general, the following preparation method is used.

When titanium tetrachloride is used as a raw material, titanium tetrachloride is dropwise added to ice-cooled water and neutralized with aqueous ammonia to form titanium hydroxide (orthotitanic acid). Then, the formed precipitate is washed with water to remove chloride ions. In such a process, when the temperature in the course of the neutralization rises to a high temperature of 20°C or higher, or the chloride ions remain in titanium oxide after washing, titanium hydroxide can be easily converted to

calcining anatase crystalline titanium oxide (for example,  
25 "KINZOKU SANKABUTU TO FUKUGO SANKABUTU" (Metal Oxides and

The titanium oxide carrier to be used in the present invention includes one having the peak intensity of the rutile crystal and that of the anatase crystal, or one having the peak intensity of the rutile crystal only. That

is, titanium oxide may be one having the diffraction peak assigned to the rutile crystal and that assigned to the anatase crystal, or one having only the diffraction peak assigned to the rutile crystal. In preferred titanium  
 5 oxide, a ratio of the peak intensity of the rutile crystal to the sum of the peak intensity of the rutile crystal and that of the anatase crystal is at least 10 %.

Specific methods for the preparation of the catalyst will be explained later in connection with the catalyst (3)  
 10 according to the first aspect of the present invention.

The supported ruthenium oxide catalyst (2) according to the first aspect of the present invention is a supported ruthenium oxide catalyst having a carbon monoxide adsorption amount of at least 87.5 ml per one gram of  
 15 ruthenium contained in the catalyst, which is measured by the steps of reducing 0.1 g of said catalyst at 220°C for 60 minutes with flowing a hydrogen gas at a flow rate of 50 ml/min. under atmospheric pressure, and conducting a metal surface area measuring method according to a carbon  
 20 monoxide pulse.

The details of the MSA measuring method will be explained in the Examples.

The adsorbed amount of carbon monoxide per the unit mass of ruthenium correlates with the metal surface area  
 25 (MSA) of ruthenium, which, in turn, correlates with the



surface area of ruthenium oxide prior to the reduction. Furthermore, the surface area of ruthenium oxide correlates with the number of active sites of catalytically active ruthenium oxide.

5           The activity of the supported ruthenium oxide catalyst corresponds to the number of active sites of ruthenium oxide, but it is difficult to directly measure the surface area of ruthenium oxide corresponding to the number of the active sites. However, it is possible to measure the metal  
10       surface area by reducing the catalyst to form metal ruthenium and then adsorbing carbon monoxide on the metal ruthenium. In this case, to maintain the correlation between the surface area of ruthenium oxide on the carrier and the surface area of metal ruthenium after the reduction,  
15       it is a prerequisite that ruthenium is not sintered by the reduction with hydrogen.

          Thus, the present inventors investigated the reducing conditions of the supported ruthenium oxide catalyst. As a result, it has been found that ruthenium oxide can be  
20       reduced without being sintered, when 220°C is selected as a reducing temperature from the range between 150°C and 250°C, one hour is selected as a reducing time, and a heating rate of 20°C/min. and a hydrogen flow rate of 50 ml/min. are  
-----  
determined.

25           The amount of carbon monoxide adsorbed on reduced

ruthenium has a specific relationship with the surface area of metal ruthenium.

Accordingly, as an index of the activity of the supported ruthenium oxide catalyst, a method for measuring the amount of adsorbed carbon monoxide has been established, which method comprises the steps of:

reducing 0.1 g of said catalyst at 220°C for 60 minutes with flowing a hydrogen gas at a flow rate of 50 ml/min. under atmospheric pressure, and

conducting a metal surface area measuring method according to a carbon monoxide pulse.

In general, the supported ruthenium oxide catalyst (2) has a carbon monoxide adsorption amount of at least 87.5 ml per one gram of ruthenium contained in the catalyst (ml/g-Ru). Preferably, the carbon monoxide adsorption amount is from 90 to 200 ml/g-Ru, more preferably from 92.5 to 150 ml/g-Ru.

Various methods may be used to prepare the supported ruthenium oxide catalyst having the larger number of active sites of ruthenium oxide. Some specific methods will be explained, but the catalyst (2) of the first aspect of the present invention can be produced by the process employed to prepare the catalyst (3) of the first aspect of the present invention.

Hereinafter, the catalyst (3) of the first aspect of

the present invention will be explained. The catalyst (3) of the first aspect of the present invention is one example of the catalyst (2) of the first aspect of the present invention.

5       The supported ruthenium oxide catalyst (3) of the first aspect of the present invention is one prepared by the process comprising the steps of:  
supporting a ruthenium compound on a carrier,

10       calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of hydrazine and an alkaline compound,

15       and

oxidizing said hydrazine-treated one.

Firstly, the step to support a ruthenium compound on a carrier is explained.

20       Examples of the carrier include oxides and mixed oxides of elements such as titanium oxide, alumina, zirconium oxide, silica, titanium mixed oxide, zirconium mixed oxide, aluminum mixed oxide, silicon mixed oxide, etc. Preferred carrier are titanium oxide, alumina, zirconium oxide and silica. Among them, titanium oxide is more  
25       preferred.

A particularly preferred carrier is titanium oxide containing rutile crystalline titanium oxide.

Such titanium oxide containing rutile crystalline titanium oxide has been explained in the above in  
5 connection with the catalyst (1) of the first aspect of the present invention.

In the case of the supported ruthenium oxide catalyst comprising titanium oxide containing rutile crystalline titanium oxide as a carrier, its catalytic activity can be  
10 increased by the optimization of the amount of OH groups contained in the carrier. In general, it is known that hydroxyl (OH) groups bonded to titanium atoms are present on the surface of titanium oxide. In the present invention, used titanium oxide contains the OH groups. A method for  
15 measuring the amount of the OH groups will be explained in detail below.

The amount of the OH groups contained in the carrier can be determined from the amount of the OH groups in titanium oxide, when the chemical composition of the  
20 carrier used in the present invention consists of titanium oxide only. However, the carrier may be a mixed oxide of titanium oxide and other metal oxide. Preferred examples of the other metal oxide include alumina, zirconium oxide, silica, etc. In such a case, the content of the metal  
25 oxide other than titanium oxide is from 0 to 60 mass %. In

this case, the amount of the OH group contained in the unit mass of the carrier can be measured by the method, which will be explained in detail below. Preferably, the carrier does not contain any metal oxide other than titanium oxide.

5           When the amount of the OH groups is too large, the carrier and supported ruthenium oxide react each other, and thus the catalyst may be deactivated. When the amount of the OH group is too small, the activity of the catalyst may be decreased by the sintering of supported ruthenium oxide  
10           or other phenomena. That is, the OH groups are contained in an amount in a suitable range depending the amount of the ruthenium compound to be supported on the carrier, and the catalytic activity gradually increases as the amount of the OH group increases in such a range, and tends to  
15           decrease after it reaches the peak activity. Therefore, the catalyst exhibits a high activity in the suitable range of the amount of the OH groups.

          The amount of the OH groups contained in the titanium oxide carrier used in the catalyst of the present invention  
20           is generally from  $0.1 \times 10^{-4}$  to  $30 \times 10^{-4}$  mol/g-carrier, preferably from  $0.2 \times 10^{-4}$  to  $20 \times 10^{-4}$  mol/g-carrier, more preferably from  $3.0 \times 10^{-4}$  to  $10 \times 10^{-4}$  mol/g-carrier.

          There are various methods for determining the amount  
-----  
of the OH groups contained in titanium oxide. A preferred  
25           method is a titration method using an alkyl alkali metal.

Preferably, the titration method using the alkyl alkali metal comprises suspending the titanium oxide carrier or the titanium oxide carrier powder in a dehydrated solvent, dropwise adding the alkyl alkali metal in a nitrogen atmosphere, and calculating the amount of the OH group contained in titanium oxide from the amount of a generated hydrocarbon. In this method, water remained in the dehydrated solvent reacts with the alkyl alkali metal to generate the hydrocarbon. Therefore, the amount of the hydrocarbon generated by the reaction of residual water and the alkyl alkali metal should be deducted from the total amount of the hydrocarbon to obtain the correct amount of the OH groups contained in titanium oxide.

In the most preferred embodiment of the above titration method, the titanium oxide carrier or the titanium oxide carrier powder is suspended in dehydrated toluene, methyl lithium is dropwise added to the suspension in the nitrogen atmosphere, and then the amount of the OH group contained in titanium oxide is calculated from the amount of generated methane. The amount of the OH groups contained in titanium oxide, which is defined in this specification, is measured by this most preferred method.

For example, the measuring steps are as follows:

Firstly, a sample is dried under air at 150°C for 2 hours, and cooled in a desiccater. Then, a specific amount

of the sample is transferred to a flask which has been replaced with nitrogen, and suspended in an organic solvent such as dehydrated toluene. Into the suspension, methyl lithium is dropwise added while cooling the flask with ice to suppress the heat generation, and the generated gas is trapped and its volume is measured at a measuring room temperature.

The process of adjusting the amount of the OH groups contained in the titanium oxide carrier to a predetermined amount includes various process. For example, a temperature and/or time to calcine the carrier can be controlled for this purpose. The OH groups can be eliminated from the titanium oxide carrier by heating, and the calcination temperature or time can be changed to control the amount of the OH groups in the titanium oxide carrier.

The calcination temperature of the carrier is usually from 100 to 1,000°C, preferably from 150 to 800°C, and the calcination time of the carrier is usually from 30 minutes to 12 hours. In the calcination step, it should be noted that the surface area of the carrier decreases as the calcination temperature rises, or the calcination time is prolonged.

Furthermore, when titanium oxide is produced in a gas phase, one containing the small amount of the OH group can

be produced, while when titanium oxide is produced in an aqueous phase such as an aqueous solution, one containing the large amount of the OH group can be produced.

Examples of the ruthenium compound to be supported on the carrier include ruthenium chlorides such as  $\text{RuCl}_3$ ,  $\text{RuCl}_3$  hydrate, etc.; chlororuthenate salts such as  $\text{K}_3\text{RuCl}_6$ ,  $(\text{RuCl}_6)^{3-}$ ,  $\text{K}_2\text{RuCl}_6$ , etc.; chlororuthenate salt hydrates such as  $[\text{RuCl}_5(\text{H}_2\text{O})_4]^{2-}$ ,  $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$ , etc.; ruthenate salts such as  $\text{K}_2\text{RuO}_4$ , etc.; ruthenium oxychlorides such as  $\text{Ru}_2\text{OCl}_4$ ,  $\text{Ru}_2\text{OCl}_5$ ,  $\text{Ru}_2\text{OCl}_6$ , etc.; salts of ruthenium oxychlorides such as  $\text{K}_2\text{Ru}_2\text{OCl}_{10}$ ,  $\text{Cs}_2\text{Ru}_2\text{OCl}_4$ , etc.; ruthenium-ammine complexes such as  $[\text{Ru}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$ , etc.; chlorides and bromides of ruthenium-ammine complexes such as  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ ,  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_2$ ,  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ ,  $[\text{Ru}(\text{NH}_3)_6]\text{Br}_3$ , etc.; ruthenium bromides such as  $\text{RuBr}_3$ ,  $\text{RuBr}_3$  hydrate, etc.; other ruthenium-organoamine complexes; ruthenium-acetylacetonato complexes; ruthenium-carbonyl complexes such as  $\text{Ru}(\text{CO})_5$ ,  $\text{Ru}_3(\text{CO})_{12}$ , etc.; organic acid salts of ruthenium such as  $[\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{H}_2\text{O})_3]\text{OCOCH}_3$  hydrate,  $\text{Ru}_2(\text{RCOO})_4\text{Cl}$  in which R is an alkyl group having 1 to 3 carbon atoms, etc.; ruthenium-nitrosyl complexes such as  $\text{K}_2[\text{RuCl}_5(\text{NO})]$ ,  $\text{Ru}[(\text{NH}_3)_5(\text{NO})]\text{Cl}_3$ ,  $[\text{Ru}(\text{OH})(\text{NH}_3)_4(\text{NO})](\text{NO}_3)_2$ ,  $\text{Ru}(\text{NO})(\text{NO}_3)_3$ , etc.; ruthenium-phosphine complexes; and the like. Preferred examples of the ruthenium compound include ruthenium halides, for example, ruthenium chlorides such as



RuCl<sub>3</sub>, RuCl<sub>3</sub> hydrate, etc., and ruthenium bromides such as RuBr<sub>3</sub>, RuBr<sub>3</sub> hydrate, etc. More preferably, ruthenium chloride hydrate is used.

The process for supporting the ruthenium compound on the carrier includes an impregnation process, an equilibrium adsorption process, etc.

Next, the calcining step is explained.

In the calcining step, the ruthenium compound-supported one, which is obtained in the previous ruthenium compound-supporting step, is calcined at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere.

Examples of the inert gas include nitrogen, helium, etc. Examples of the oxidizing gas include air, oxygen, a mixture of nitrogen and oxygen, etc. Examples of the reducing gas include hydrogen, a mixture of hydrogen and nitrogen, etc.

In this step, the ruthenium compound-supported one is dried, and then the ruthenium compound is fixed on the carrier, so that the ruthenium compound can be stably treated in the subsequent hydrazine-treating step.

When the catalyst produced by the process including this calcination step is compared with a catalyst produced by the same process but including no calcination step, the

treatment with hydrazine is considerably stably conducted, so that the catalytic activity increases. Preferably, the ruthenium compound-supported one is calcined in the oxidizing gas atmosphere, more preferably, under air.

5 Hereinafter, the hydrazine-treating step is explained.

The hydrazine-treating step includes that the calcined one from the previous calcination step is treated with hydrazine by dipping the calcined one in a mixed solution of hydrazine and an alkali, or impregnating the calcined  
10 one with such a mixed solution.

Examples of the alkali to be used include aqueous solutions of hydroxides, carbonates or hydrogen carbonates of alkali metals, ammonia, ammonium carbonate, ammonium hydrogen carbonate, etc.; solutions of these alkali  
15 compounds in organic solvents such as alcohol; and the like.

Preferred examples of the alkali include hydroxides, carbonates and hydrogen carbonates of alkali metals. Preferred examples of the solvent include water.

In addition, except treating with hydrazine, another  
20 preferred method is exemplified. Another preferred method comprises reducing the calcined one from the calcination step, in a liquid phase.

Examples of reducing agents include methanol or formaldehyde; aqueous solutions and organic solvent  
25 solutions of methanol or formaldehyde; hydrogen; boron

hydride compounds such as  $\text{NaBH}_4$ ,  $\text{Na}_2\text{B}_2\text{H}_6$ ,  $\text{Na}_2\text{B}_4\text{H}_{10}$ ,  $\text{Na}_2\text{B}_5\text{H}_9$ ,  
 $\text{LiBH}_4$ ,  $\text{K}_2\text{B}_2\text{H}_6$ ,  $\text{K}_2\text{B}_4\text{H}_{10}$ ,  $\text{K}_2\text{B}_5\text{H}_9$ ,  $\text{Al}(\text{BH}_4)_3$ , etc.; organometallic  
boron hydride compounds such as  $\text{LiB}[\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5]_3\text{H}$ ,  
 $\text{LiB}(\text{C}_2\text{H}_5)_3\text{H}$ ,  $\text{KB}[\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5]_3\text{H}$ ,  $\text{KB}[\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2]_3\text{H}$ , etc.;  
5 metal hydrides such as  $\text{LiAlH}_4$ ,  $\text{NaH}$ ,  $\text{LiH}$ ,  $\text{KH}$ , etc.;  
organoaluminum compounds such as  $[(\text{CH}_3)_2\text{CHCH}_2]_2\text{Al}$ , etc.;  
organolithium compounds; organosodium compounds;  
organopotassium compounds; organomagnesium compounds; and  
the like.

10 It is also preferable to add an alkali metal chloride  
after the treatment with hydrazine or the reducing agent.

The oxidizing process includes a process comprising  
calcining the treated one under air.

A weight ratio of ruthenium oxide to the carrier is  
15 preferably from 0.1:99.9 to 20.0:80.0, more preferably from  
0.5:99.5 to 15.0:85.0, in particular from 1.0:99.0 to  
15.0:85.0.

When the ratio of ruthenium oxide is too low, the  
activity of the produced catalyst may decrease. When the  
20 ratio of ruthenium oxide is too high, the cost of the  
catalyst may increase.

Ruthenium oxide is preferably ruthenium dioxide or  
ruthenium oxide hydrates. Alternatively, ruthenium  
hydroxide may be used as a precursor of ruthenium oxide.

25 A preferable example of the process for preparing the

supported ruthenium oxide catalyst (3) of the first aspect of the present invention is a process comprising the steps of:

supporting a ruthenium halide on a carrier,

5 calcining the supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

10 treating the calcined one with a mixed solution of hydrazine and an alkaline compound, and

oxidizing the hydrazine-treated one.

A more preferable example of the process for preparing the supported ruthenium oxide catalyst (3) of the first aspect of the present invention is a process comprising the steps of:

supporting a ruthenium halide on a carrier,

20 calcining the supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

treating the calcined one with a mixed solution of hydrazine and an alkaline compound,

25 adding an alkali metal halide to the hydrazine-treated one,

and

oxidizing the alkali metal halide-added one.

In the first step of the above preferred embodiment, a ruthenium halide is supported on a carrier.

5       As the ruthenium halides, those exemplified in the above may be used. Among them, ruthenium chlorides such as  $\text{RuCl}_3$ ,  $\text{RuCl}_3$  hydrate and ruthenium bromide such as  $\text{RuBr}_3$ ,  $\text{RuBr}_3$  hydrate are preferred. In particular, ruthenium chloride hydrate is preferred.

10       The amount of the ruthenium halide to be used in the step for supporting the ruthenium halide on the carrier is an amount satisfying a preferred weight ratio of ruthenium oxide to the carrier.

15       The ruthenium halide may be supported on the carrier by impregnating the catalyst carrier, which is explained in the above, with the solution of the ruthenium halide, or supporting the ruthenium halide on the carrier by the equilibrium absorption.

20       As a solvent, water or an organic solvent such as an alcohol is used. Preferably, water is used.

25       Next, the impregnated carrier may be dried or may not be dried. Preferably, it is dried. This drying is carried out to remove the solvent from the impregnated solution of the ruthenium halide, and it has the different purpose from the subsequent calcination and should be distinguished from

In the hydrazine-treating step, the product from the calcination step is treated with the mixed solution of hydrazine and an alkali. The treatment with the mixed solution of hydrazine and the alkali can be carried out by dipping the calcined one in such a mixed solution, or

impregnating the carrier with such a mixed solution.

The concentration of hydrazine used in the hydrazine-treating step is preferably at least 0.1 mol/l. Hydrazine is used in the form of a solution in water or an organic solvent such as an alcohol, while hydrazine hydrate such as hydrazine monohydrate may be used as such. Preferably, the aqueous solution of hydrazine, or hydrazine hydrate is used. Hydrazine may be anhydrous hydrazine or hydrazine hydrate.

A molar ratio of the ruthenium halide to hydrazine is preferably from 1:0.1 to 1:20. In the case of sodium hydroxide, 3 moles of sodium hydroxide per one mole of the ruthenium halide is an equimolar amount. Preferably, the alkali is used in the amount of 0.1 to 20 equivalent per equivalent of ruthenium halide.

The concentration of the alkali varies with the kind of the alkali, and is preferably from 0.1 to 10 mol/l.

The time to dip the calcined product in the mixed solution of hydrazine and the alkali is preferably from 5 minutes to 5 hours. The dipping temperature is preferably from 0 to 100°C, more preferably from 10 to 60°C. After dipping, the treated product is filtrated to separate the solution.

In a preferred embodiment of the above process, the product from the hydrazine-treating step is washed with water to remove the alkali and hydrazine, dried, and then

added with an alkali metal chloride in the subsequent step to add the alkali metal chloride, followed by drying and oxidizing.

In a more preferred embodiment, the product from the hydrazine-treating step is washed with an aqueous solution of an alkali metal chloride, dried and then oxidized. In this embodiment, the removal of the alkali and hydrazine and the addition of the alkali metal chloride can preferably be carried out in the same step.

In the alkali metal chloride-adding step, the alkali metal chloride is added to the product from the hydrazine-treating step. This step may not be essential to the preparation of the supported ruthenium oxide catalyst, but this step can further increase the activity of the catalyst. That is, in the subsequent oxidizing step, the hydrazine-treated catalyst is oxidized in the presence of the alkali metal chloride to obtain the supported ruthenium oxide catalyst having the higher activity.

Examples of the alkali metal chloride include potassium chloride, sodium chloride, etc. Preferably, potassium chloride or sodium chloride is used, and more preferably potassium chloride is used.

A molar ratio of the alkali metal chloride to ruthenium is preferably from 0.01:1 to 10:1, more preferably from 0.1:1 to 5.0:1. When the amount of the





of 1 to 10 hours.

The oxidation step is a step for oxidizing the product from the hydrazine-treating step (when the step to add the alkali metal chloride is not used), or a step for oxidizing the product from the alkali metal chloride-adding step (when the step to add the alkali metal chloride is used).

It is a preferable preparation example to convert it into highly active supported ruthenium oxide by calcining one treated with the alkali and hydrazine in the presence of an alkali metal salt, in a gas containing oxygen. An example of the oxygen-containing gas is usually an air.

The calcination temperature is preferably from 100 to 600°C, more preferably from 280 to 450°C. When the calcination temperature is too low, many particles generated by the treatment with hydrazine may remain in the form of a ruthenium oxide precursor and thus the obtained catalyst may have an insufficient activity. When the calcination temperature is too high, the ruthenium oxide particles tend to agglomerate, so that the catalytic activity deteriorates.

The calcination time is preferably from 30 minutes to 10 hours.

In this step, it is preferable and important to carry out the calcination in the presence of the alkali metal chloride. By this method, ruthenium oxide having a smaller

particle size is obtained, so that the higher catalytic activity is achieved than a catalyst prepared by the calcination substantially in the absence of the alkali metal chloride.

5 By the calcination, the particles supported on the carrier, which have been generated by the treatment with hydrazine, are converted to the supported ruthenium oxide catalyst.

10 The conversion of the particles generated by the treatment with hydrazine to ruthenium oxide can be confirmed by an analysis such as X-ray diffraction, XPS (X-ray photoelectron spectroscopy), etc.

15 In the particles generated by the treatment with hydrazine, preferably, substantially all the particles are converted to ruthenium oxide, although some particles may remain unconverted insofar as the effects of the present invention are not impaired.

20 In addition, in a preferred embodiment, after the oxidation step, the catalyst is washed with water to remove the residual alkali metal chloride, and dried. It is preferable to thoroughly wash off the alkali metal chloride which is present in the oxidation step.

25 The residual amount of the alkali metal chloride after washing can be measured by adding an aqueous solution of silver nitrate and checking the formation of white

turbidity. The alkali metal chloride may remain in the catalyst to an extent such that the activity of the catalyst of the present invention may not be deteriorated.

Preferably, the washed catalyst is dried. Preferably,  
5 the drying conditions include a temperature of 50 to 200°C, and a time of 1 to 10 hours.

The supported ruthenium oxide catalyst, which is prepared by the above-described process has a high activity and is more active than a catalyst prepared by reducing  
10 ruthenium chloride with hydrogen and oxidizing it. Furthermore, the catalyst, which is obtained by pretreating the ruthenium compound with the alkali, treating the product with hydrazine, and then oxidizing the hydrazine-treated product, has a higher activity than a catalyst  
15 prepared by treating ruthenium chloride with hydrazine and oxidizing the hydrazine-treated product.

Hereinafter, the process for producing the supported ruthenium oxide catalyst or a supported ruthenium chloride catalyst of the second aspect of the present invention is  
20 explained.

The process (1) of the second aspect of the present invention comprises the steps of:

supporting a ruthenium compound on a carrier consisting of titanium oxide which contains the rutile  
25 crystal form, and which is obtained by calcination at a

temperature of at least 550°C, and

calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere.

5 The detailed explanation of this process is already made in connection with the catalyst (1) of the first aspect of the present invention.

Next, the process (2) of the second aspect of the present invention comprises the steps of:

10 supporting a ruthenium compound on a carrier,

calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

15 treating said calcined one with a mixed solution of hydrazine and an alkaline compound, and

oxidizing said hydrazine-treated one wherein said supported ruthenium oxide catalyst has a  
20 carbon monoxide adsorption amount of at least 87.5 ml per one gram of ruthenium contained in the catalyst, which is measured by the following steps of:

reducing 0.1 g of said catalyst at 220°C for 60  
minutes with flowing a hydrogen gas at a flow rate of 50  
25 ml/min. under atmospheric pressure, and

conducting a metal surface area measuring method  
according to a carbon monoxide pulse.

The detailed explanation of this process is already  
made in connection with the catalysts (2) and (3) of the  
5 first aspect of the present invention.

The process (3) of the second aspect of the present  
invention comprises the steps of:

supporting a ruthenium compound on a carrier,

10 calcining said supported one at a temperature of at  
least 200°C in an atmosphere selected from the group  
consisting of an oxidizing gas atmosphere, an inert gas  
atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of  
hydrazine and an alkaline compound,

15 and

oxidizing said hydrazine-treated one.

The detailed explanation of this process is already  
made in connection with the catalyst (3) of the first  
aspect of the present invention.

20 The process (4) of the second aspect of the present  
invention comprises the steps of:

supporting a ruthenium compound on a carrier,

and

25 calcining said supported one in an atmosphere selected  
from the group consisting of an oxidizing gas atmosphere,

an inert gas atmosphere and a reducing gas atmosphere,  
wherein, when the peak intensity ratio of the produced  
catalyst and that of the catalyst after a 50 hours reaction  
test, which are measured by an extended X-ray absorption  
5 fine structure analysis (EXAFS) method, are A(b) and B(b)  
respectively, the peak intensity ratios A(b) and B(b)  
satisfy the following equation (1):

$$1 \leq B(b)/A(b) \leq 1.45 \quad (1)$$

provided that  $A(b) \leq 0.8$ ,

10 wherein A(b) is a peak intensity ratio of as-produced  
Catalyst b measured by the EXAFS method, and B(b) is a peak  
intensity ratio of Catalyst b measured by the EXAFS method  
after the 50 hours reaction test;  
in which

15 the 50 hours reaction test is carried out by filling  
supported ruthenium oxide Catalysts a and b in a reactor in  
this order from the inlet of the reactor in a weight ratio  
of 1:10 (Catalyst a to Catalyst b), and supplying, under  
atmospheric pressure, a hydrogen chloride gas at a flow  
20 rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an  
oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr.  
to carry out the reaction for 50 hours while maintaining  
the hot spot of Catalyst b at  $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , wherein Catalyst a  
is a catalyst having a chlorine formation activity per unit  
25 mass of catalyst of  $2 \times 10^{-4}$  to  $3 \times 10^{-4}$  mol/min.g-cat.,

which is obtained in a reaction test for forming chlorine  
by oxidizing hydrogen chloride with oxygen at 300°C with a  
molar ratio of hydrogen chloride to oxygen being 1:1, and  
Catalyst b is a supported ruthenium oxide Catalyst produced  
5 by the above process,  
and in which

EXAFS method: Catalyst b is measured by an X-ray  
absorption fine structure analysis (XAFS) method at the Ru-  
K absorption edge, and the peak intensity of the catalyst  
10 is evaluated by the peak around 0.32 nm in a radial  
distribution function obtained by the Fourier  
transformation of the EXAFS spectrum, wherein the peak  
intensity corresponds to the number of the second nearest  
neighbor ruthenium atoms of the X-ray absorbing ruthenium  
15 atoms in ruthenium dioxide, and the peak intensity ratio of  
the catalyst is calculated by dividing the peak intensity  
of the catalyst by that of ruthenium oxide having a  
particle size of at least 10 nm.

The reaction test for forming chlorine, which is  
20 carried out by oxidizing hydrogen chloride with oxygen at  
300°C with a molar ratio of hydrogen chloride to oxygen  
being 1:1, may be conducted as follows:

The supported ruthenium oxide catalyst (2.5 g) is well  
mixed with a commercially sold spherical  $\alpha$ -alumina carrier  
25 having a diameter of 2 mm (SSA 995 manufactured by NIKKATO



Co., Ltd.) (10 g) to dilute the catalyst, and then charged in a quartz reactor tube having an inner diameter of 12 mm. In the reactor tube, hydrogen chloride gas and oxygen gas are supplied at flow rates of 192 ml/min. and 192 ml/min., respectively (each converted to a volume at 0°C under 1 atm.)

The quartz reactor tube is heated with an electric furnace to adjust the internal temperature (hot spot) to 300°C.

When 2 hours lapses from the start of the reaction, the gas from the outlet of the reactor tube is sampled by passing it through an aqueous 30 mass % potassium iodide solution, and the amount of chlorine formed and the amount of unreacted hydrogen chloride are determined by iodometric titration and neutralization titration, respectively.

Then, a chlorine formation activity per unit mass of the catalyst is calculated according to the following equation:

$$\text{Chlorine formation activity (mol/min.g-cat.)} = \frac{\text{Amount of outlet chlorine formed per unit time (mol/min.)}}{\text{weight of catalyst (g)}}$$

Furthermore, it has been found that the peak intensity ratio of the supported ruthenium oxide catalyst, which is explained below, corresponds to the structure of ruthenium oxide supported on the carrier and correlates with the

catalyst activity. The peak intensity ratio is obtained by dividing the peak intensity corresponding to the number of the second nearest neighbor ruthenium atoms of the X-ray absorbing ruthenium atoms in ruthenium dioxide carried on the support which is measured by the EXAFS method (a numerator) by the peak intensity of ruthenium oxide having a particle size of at least 10 nm (a denominator).

That is, when the peak intensity ratio of the spectrum corresponding to the number of the second nearest neighbor ruthenium atoms of ruthenium atoms in ruthenium dioxide, which is obtained from the peak intensity around 0.32 nm in a radial distribution function, is used and the form of ruthenium dioxide is assumed, the size of the ruthenium dioxide block can be obtained. In this case, the preferable size of the ruthenium dioxide block depends on the assumed form of ruthenium dioxide. When the peak intensity ratio is calculated with the peak intensity of the spectrum corresponding to the number of the second nearest neighbor ruthenium atoms of ruthenium atoms in ruthenium dioxide being a numerator, and the peak intensity of ruthenium oxide having the particle size of 10 nm or more being a denominator, the peak intensity ratio of 0.8 or less correspond to the size of the ruthenium dioxide block desirable for the supported ruthenium oxide catalyst of the present invention.

Furthermore, when the peak intensity ratio of the catalyst prior to the reaction is compared with that of the catalyst after the reaction, the change of the size of the ruthenium dioxide block can be monitored, and thus the progress of the sintering of ruthenium oxide on the carrier can be measured.

That is, in one preferred embodiment, the present invention provides a process for producing a catalyst in which the ratio of the above defined peak intensity ratio before the reaction to that after the reaction is 1.45 or less. The specific procedures of such a process will be explained below.

One of the characteristics of the catalyst according to the present invention is that ruthenium oxide is less sintered when the above-defined specific ruthenium oxide catalyst is used in the production process of the desired product, that is, chlorine using a supported ruthenium oxide catalyst.

In the present invention, the above-defined ratio  $B(b)/A(b)$  is preferably 1.40 or less, more preferably 1.25 or less.  $A(b)$  is preferably 0.7 or less.

Here, a general procedure of the X-ray absorption fine structure analysis (XAFS) method is explained. The principle and analysis method of XAFS are described in detail in, for example, X-Ray Absorption. Principles,

Applications, Techniques of EXAFS, SEXAFS and XANES" edited by D.C. Koningsberger and R. Prins (1988).

When a material is placed on a beam line of X-ray, an X-ray absorbanace of the material is calculated from the intensity of the irradiated X-ray (incident X-ray:  $I_0$ ) and the intensity of X-ray which passes through the material (transmitted X-ray:  $I_t$ ). When an X-ray absorption spectrum is recorded while the energy of X-ray is changed with monitoring the increase or decrease of the X-ray absorbance, an abrupt standing of the X-ray absorbance (absorption edge) is observed at a certain X-ray energy level. Fine oscillatory structures, which appear in the range on the high energy side that is about 30 to 1,000 eV higher than the energy of the absorption edge, are extended X-ray absorption fine structures. The fluctuation of the X-ray absorption probability is caused by the interference between photoelectron waves emitted from the absorbing atom by the absorption of X-ray and photoelectron waves which are scattered by and returning from atoms surrounding the absorbing atom. Thus, the information on the local structure near the absorbing atom can be obtained when the fluctuation of the X-ray absorption probability is extensively analyzed.

A radial distribution function around the X-ray absorbing atom is obtained, when the EXAFS spectrum, which

is extracted from the X-ray absorption spectrum is subjected to the Fourier transformation in a suitable range. When this radial distribution function is examined in detail, the position of the maximum of this function provides the information on the distance between the absorbing atom and the scattering atom, and the intensity of the maximum provides the information on the number of the scattering atoms. Thus, the structural information near the noted absorbing atom can be gathered.

Hereinafter, the concrete procedures of the process (4) of the second aspect of the present invention will be explained. The process (4) comprises the steps of supporting a ruthenium compound on a carrier, and calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere.

Firstly, the step to support a ruthenium compound on a carrier is explained.

As a carrier, the same carrier as that used in the process (3) of the second aspect of the present invention can be used.

Titanium oxide containing rutile crystalline titanium oxide, which is preferably used in the present invention, means titanium oxide containing the rutile crystal, when the ratio of the rutile crystal to the anatase crystal in

titanium oxide is measured by the X-ray diffraction analysis. This analysis is explained in connection with the catalyst (1) of the first aspect of the present invention.

5 Titanium oxide should contain the rutile crystal. The proportion of the rutile crystal is preferably at least 10 %, more preferably at least 30 %, in particular at least 80 %.

10 In one preferred embodiment, titanium oxide contains OH groups in an amount which is explained in connection with the catalyst (3) of the first aspect of the present invention.

The ruthenium compound to be supported on the carrier may be the same as those exemplified in connection with the catalyst (3) of the first aspect of the present invention. Preferred examples of the ruthenium compound include ruthenium halides, for example, ruthenium chlorides such as  $\text{RuCl}_3$ ,  $\text{RuCl}_3$  hydrate, etc., and ruthenium bromides such as  $\text{RuBr}_3$ ,  $\text{RuBr}_3$  hydrate, etc. More preferably, ruthenium chloride hydrate is used.

15  
20

The process for supporting the ruthenium compound on the carrier includes an impregnation process, an equilibrium adsorption process, etc.

The calcination is preferably carried out in an air.

25 A weight ratio of ruthenium oxide to the carrier is

preferably from 0.1:99.9 to 20.0:80.0, more preferably from 0.5:99.5 to 15.0:85.0, in particular from 1.0:99.0 to 15.0:85.0.

When the ratio of ruthenium oxide is too low, the activity of the produced catalyst may decrease. When the ratio of ruthenium oxide is too high, the cost of the catalyst may increase.

Ruthenium oxide is preferably ruthenium dioxide. Alternatively, ruthenium hydroxide may be used as a precursor of ruthenium oxide.

In one preferable embodiment of the process (4) of the second aspect, the catalyst is prepared by a process comprising the steps of:

supporting a ruthenium halide on a carrier,  
and

calcining the supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere.

As the ruthenium halides, those exemplified in the above may be used. Among them, ruthenium chlorides such as  $\text{RuCl}_3$ ,  $\text{RuCl}_3$  hydrate and ruthenium bromide such as  $\text{RuBr}_3$ ,  $\text{RuBr}_3$  hydrate are preferred. In particular, ruthenium chloride hydrate is preferred.

In the calcining step, the ruthenium halide-supported

one, which is obtained in the previous ruthenium halide-supporting step, is calcined at a temperature of at least 200°C in an atmosphere selected from the group consisting an oxidizing gas atmosphere, an inert gas atmosphere and a  
5 reducing gas atmosphere.

Examples of the inert gas include nitrogen, helium, etc. Examples of the oxidizing gas include air, oxygen, a mixture of nitrogen and oxygen, etc. Examples of the reducing gas include hydrogen, a mixture of hydrogen and  
10 nitrogen, etc. Among them, the air is preferable.

Preferably, the ruthenium halide-supported one is calcined and oxidized in the atmosphere containing oxygen to form supported ruthenium oxide having a higher activity. The atmosphere containing oxygen is usually the air.

15 The calcination temperature is preferably from 250 to 600°C, more preferably from 250 to 450°C, particularly preferably from 250 to 400°C. When the calcination temperature is too low, a large amount of ruthenium compound remains unoxidized and thus the obtained catalyst  
20 may have an insufficient activity. When the calcination temperature is too high, the ruthenium oxide particles tend to agglomerate, so that the catalytic activity deteriorates.

The calcination time is preferably from 30 minutes to 10 hours.

25 Preferably, substantially all the particles, which are



generated in the oxidizing step are converted to ruthenium oxide, although some particles may remain unconverted insofar as the effects of the present invention are not impaired.

5           Hereinafter, a reaction process for producing chlorine by oxidizing hydrogen chloride using Catalyst b to measure B(b) is explained.

          As a material of a test reaction tube, nickel, glass, quartz glass, and the like can be used. Since feed gasses  
10           and formed gasses are corrosive, some special cares should be taken when other material is used. When the catalysts a and b to be filled in the reactor tube have a high activity, the heat of reaction cannot be removed from the reaction tube. In such a case, each catalyst is diluted with a  
15           carrier such as  $\alpha$ -alumina balls and then filled in the reaction tube to increase the heat-removing efficiency. When the heat conductivity of the catalyst layers in the reactor tube is insufficient, the heat of reaction is not removed and thus the temperature locally rises and the  
20           reaction temperature may not be suitably controlled so that the correct test may not be performed. The temperature of a hot spot set in the Catalyst b layer should be  $360 \pm 1^\circ\text{C}$ . In general, a temperature distribution is formed in the catalyst a layer and the catalyst b layer. Thus, the  
25           temperature in each catalyst layer is from 320 to  $360^\circ\text{C}$

during the reaction. When the reaction temperature is too high,  $\text{RuO}_2$ , which is a catalytically active site, quickly agglomerates, and therefore B(b) may not be measured correctly. When the reaction temperature is too low,  $\text{RuO}_2$ , which is a catalytically active site, slowly agglomerates, and thus B(b) may not be measured correctly. When the reaction is carried out by taking the above points into account, the test results can be obtained with good reproducibility.

In the preferable supported ruthenium oxide catalyst, the peak intensity ratios A(b) and B(b) satisfy the following equation:

$$1 \leq B(b)/A(b) \leq 1.45$$

in which A(b) and B(b) are the same as defined in the above explanation of the measuring by the EXAFS method. As already described, it has been found that the above peak intensity ratio has the relationship with the structure of ruthenium oxide supported on the carrier. In addition, it has been found that the stability of the peak intensity ratio, which is represented by  $B(b)/A(b)$ , correlates with the stability of the catalytic activity, wherein A(b), B(b) are the peak intensity ratios measured by the EXAFS method as already described above.

That is, the sintering of ruthenium dioxide in the catalyst is less, as the  $B(b)/A(b)$  is smaller.

In the case of the catalyst (3) of the first aspect of the present invention, the catalyst is obtained by main four preparation processes comprising the steps of: supporting process, calcining process, hydrazine-treating process and oxidizing process. In addition to these four process, alkali metal chloride-adding process, washing process and drying process were added to the catalyst preparation process resulted in establishing the catalyst preparation process which has many processes. From the viewpoint of the convenient preparation of catalysts, a process comprising the steps of supporting process and calcining process is very short catalyst preparation process which is comprised by two processes. The above process is preferred because the time of catalyst preparation is short and a preparation cost decrease. Moreover, the above catalysts were more active than the catalyst which was prepared by oxidizing the ruthenium catalyst prepared by hydrogenation of supported ruthenium chloride on a carrier by hydrogen.

Next, the process (5) of the second aspect of the present invention is explained. This process comprises the following steps but not a treating step with hydrazine:

supporting a ruthenium compound on a titanium oxide carrier containing the rutile crystal form,  
and

calcining said supported one at a temperature of 200°C to 600°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere.

5 In one preferred embodiment of the process (5), the catalyst is prepared by a process comprising the following steps but not a treating step with hydrazine:

supporting a ruthenium compound on a carrier,  
and

10 calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, wherein the catalytic activity value of the produced catalyst and the catalytic activity value of the catalyst  
15 after 50 hours reaction test, which are measured by a catalytic activity test which is defined below, are respectively C(b) and D(b), and which satisfy the following equation (2):

$$0.79 \leq D(b)/C(b) \leq 1 \quad (2)$$

20 provided that  $C(b) \geq 3.0 \times 10^{-4}$  mol/min·g-cat  
wherein C(b) is a catalytic activity value of the produced catalyst b, which is measured by the catalytic activity test and D(b) is a catalytic activity value of the catalyst b, which is measured by the catalytic activity test after a  
25 50 hours reaction test;

in which

the 50 hours reaction test is carried out by filling supported ruthenium oxide Catalysts a and b in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and supplying, under atmospheric pressure, a hydrogen chloride gas at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at  $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , wherein Catalyst a is a catalyst having a chlorine formation activity per unit mass of catalyst of  $2 \times 10^{-4}$  to  $3 \times 10^{-4}$  mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at  $300^{\circ}\text{C}$  with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide catalyst produced by the above process, and in which

Catalytic activity test: 2.3 to 2.5 grams of a catalyst is diluted by mixing with 10 to 20 g of a spherical  $\alpha$ -alumina carrier having a diameter of 2 mm, and filled in a quartz reactor tube having an inner diameter of 12 mm, then a hydrogen chloride gas and an oxygen gas are supplied in the reactor under atmospheric pressure at flow rates of 190 to 210 ml/min. and 190 to 210 ml/min.,

respectively (both volumes being converted to those at 0°C  
under 101 kPa) while heating the reactor in an electric  
furnace and maintaining the internal temperature (hot spot)  
at 300±1°C, after 2.0±1.0 hours from the start of the  
5 reaction, an exit gas from the reactor is sampled by  
passing it through a 30 mass % aqueous solution of  
potassium iodide, the amount of formed chlorine and the  
amount of unreacted hydrogen chloride are measured by an  
iodine titration method and a neutralization titration  
10 method, respectively, and thereafter a chlorine formation  
activity per unit mass of the catalyst is calculated by the  
following equation and used as a catalyst activity:  
Chlorine formation activity per unit mass of the catalyst  
(mol/min.g-cat.) =  
15 Amount of chlorine gas from reactor exit (mol/min.)/  
catalyst weight (g).

Hereinafter, the concrete procedures of the process  
(5) of the second aspect of the present invention will be  
explained.

20 The ruthenium compound may be supported on the carrier  
by the same supporting method as that explained in  
connection with the processes (3) and (4) of the second  
aspect of the present invention. The carrier may be a  
titanium oxide carrier containing the rutile crystal, which  
25 is explained in connection with the catalyst (1) of the

first aspect of the present invention.

The calcination step may be carried out in the same way as that explained in connection with the process (4) of the second aspect of the present invention. That is, this process is characterized in that the ruthenium compound-  
5 supported one is calcined at a temperature of 200 to 600°C and carried out in an oxidizing gas atmosphere, an inert gas atmosphere or a reducing gas atmosphere.

The preferable calcination temperature may be the same  
10 as that explained in connection with the process (4) of the second aspect of the present invention.

The catalyst prepared by the process (5) is characterized in that it suffers from less deactivation in the catalytic activity test when the 50 hours reaction test  
15 is carried out at a temperature of  $360 \pm 1^\circ\text{C}$ . That is, the D(b)/C(b) ratio, which is defined in the above, is at least 0.79, preferably at least 0.81, more preferably at least 0.84.

C(b) is usually at least 3.0, preferably at least 3.5.

20 The supported ruthenium oxide catalyst prepared by the process (4) has a high catalytic activity.

The process (6) of the second aspect of the present invention comprises the following steps but neither a calcining step nor a treating step with hydrazine:

25 supporting a ruthenium halide on a titanium oxide

carrier containing the rutile crystal form,  
and

drying said supported one in an atmosphere selected  
from the group consisting of an oxidizing gas atmosphere,  
5 an inert gas atmosphere and a reducing gas atmosphere at a  
temperature of 20°C to less than 200°C.

In one preferable embodiment of the process (6) of the  
second aspect of the present invention, the catalyst is  
prepared by a process comprising the following steps but  
10 neither a calcining step nor a treating step with  
hydrazine:

supporting a ruthenium halide on a titanium oxide  
carrier containing the rutile crystal form,  
and

15 drying said supported one in an atmosphere selected  
from the group consisting of an oxidizing gas atmosphere,  
an inert gas atmosphere and a reducing gas atmosphere at a  
temperature of 20°C to less than 200°C,  
wherein the catalytic activity value of the produced  
20 catalyst and the catalytic activity value of the catalyst  
after 50 hours reaction test, which are measured by a  
catalytic activity test which is defined below, are  
respectively E(b) and F(b), and which satisfy the following  
equation (3);

25 
$$0.80 \leq F(b)/E(b) \leq 1.20 \quad (3)$$



provided that  $E(b) \geq 3.0 \times 10^{-4}$  mol/min.g-cat.,  
in which

50 Hours reaction test: Supported ruthenium oxide  
Catalysts a and b are filled in a reactor in this order  
5 from the inlet of the reactor in a weight ratio of 1:10  
(Catalyst a to Catalyst b), and a hydrogen chloride gas is  
supplied under atmospheric pressure at a flow rate of 0.185  
to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a  
flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the  
10 reaction for 50 hours while maintaining the hot spot of  
Catalyst b at  $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , in which Catalyst a is a supported  
ruthenium oxide catalyst having a chlorine formation  
activity per unit mass of the catalyst of  $2 \times 10^{-4}$  to  $3 \times$   
 $10^{-4}$  mol/min.g-cat., which is obtained in a reaction test  
15 for forming chlorine by oxidizing hydrogen chloride with  
oxygen at  $300^{\circ}\text{C}$  with a molar ratio of hydrogen chloride to  
oxygen being 1:1, and Catalyst b is a supported ruthenium  
oxide catalyst produced by the above process,  
and in which

20 Catalytic activity test: 2.3 to 2.5 grams of a  
catalyst is diluted by mixing with 10 to 20 g of a  
spherical  $\alpha$ -alumina carrier having a diameter of 2 mm, and  
filled in a quartz reactor tube having an inner diameter of  
12 mm, then a hydrogen chloride gas and an oxygen gas are  
25 supplied in the reactor under atmospheric pressure at flow

rates of 190 to 210 ml/min. and 190 to 210 ml/min.  
 respectively (both volumes being converted to those at 0°C  
 under 101 kPa) while heating the reactor in an electric  
 furnace and maintaining the internal temperature (hot spot)  
 at 300±1°C, after 2.0±1.0 hours from the start of the  
 reaction, an exit gas from the reactor is sampled by  
 passing it through a 30 mass % aqueous solution of  
 potassium iodide, the amount of formed chlorine and the  
 amount of unreacted hydrogen chloride are measured by an  
 iodine titration method and a neutralization titration  
 method, respectively, and thereafter a chlorine formation  
 activity per unit mass of the catalyst is calculated by the  
 following equation and used as a catalyst activity:

Chlorine formation activity per unit mass of the catalyst  
 (mol/min.g-cat.) =  
 Amount of chlorine gas from reactor exit (mol/min.)/  
 catalyst weight (g).

The catalyst prepared by the process (6) is  
 characterized in that it suffers from less deactivation in  
 the catalytic activity test when the 50 hours reaction test  
 is carried out at a temperature of 360±1°C. That is, the  
 F(b)/E(b) ratio, which is defined in the above, is at least  
 0.80, preferably at least 0.83, more preferably at least  
 0.85.

E(b) is usually at least 3.0, preferably at least 3.5.

Hereinafter, the concrete procedures of the process (6) of the second aspect of the present invention will be explained.

Firstly, the step to support the ruthenium halide on the carrier is explained. The carrier may be the same as that exemplified in connection with the catalyst (1) of the first aspect of the present invention. That is, titanium oxide containing rutile crystalline titanium oxide, which is preferably used in the present invention, means titanium oxide containing the rutile crystal, when the ratio of the rutile crystal to the anatase crystal in titanium oxide is measured by the X-ray diffraction analysis. This analysis is explained in connection with the catalyst (1) of the first aspect of the present invention.

Titanium oxide should contain the rutile crystal. The proportion of the rutile crystal is preferably at least 10 %, more preferably at least 30 %, in particular at least 80 %.

As the ruthenium halides, those exemplified in the connection with the catalyst (3) of the first aspect of the present invention may be used. Preferable examples of the ruthenium halides include ruthenium chlorides such as  $\text{RuCl}_3$ ,  $\text{RuCl}_3$  hydrate; ruthenium bromide such as  $\text{RuBr}_3$ ,  $\text{RuBr}_3$  hydrate; and ruthenium oxychlorides such as  $\text{Ru}_2\text{OCl}_4$ ,  $\text{Ru}_2\text{OCl}_5$ . In particular, ruthenium chloride hydrate is preferred.

That is, in the present invention, ruthenium (III) chloride,  
ruthenium (III) chloride hydrate or a compound obtained by  
dissolving ruthenium (III) chloride hydrate in water and  
spontaneously hydrolyzing it may be used. Furthermore,  
5 ruthenium (III) bromide, ruthenium (III) bromide hydrate or  
a compound obtained by dissolving ruthenium (III) bromide  
hydrate in water and spontaneously hydrolyzing it may be  
used. More preferably, ruthenium chloride hydrate is used.

The process for supporting the ruthenium halide on the  
10 carrier includes an impregnation process, an equilibrium  
adsorption process, etc.

The carrier supporting the ruthenium halide is dried  
under air or nitrogen.

A weight ratio of ruthenium oxide to the carrier is  
15 preferably from 0.15:99.85 to 31.2:68.8, more preferably  
from 0.8:99.2 to 23.4:76.6, particularly preferably from  
1.6:98.4 to 23.4:76.6. When the ratio of ruthenium halide  
is too low, the activity of the produced catalyst may  
decrease. When the ratio of ruthenium halide is too high,  
20 the cost of the catalyst may increase.

In the drying step, the carrier supporting the  
ruthenium halide is dried at a temperature of 20 to 200°C  
in an oxidizing gas atmosphere, an inert gas atmosphere or  
a reducing gas atmosphere. Examples of the inert gas  
25 include nitrogen, helium, etc. Examples of the oxidizing

As a material of a test reaction tube, nickel, glass, quartz glass, and the like can be used. Since reaction gasses and formed gasses are corrosive, some special cares should be taken when other material is used. When the catalysts a and b to be filled in the reactor tube have a high activity, the heat of reaction cannot be removed from

the reaction tube. In such a case, each catalyst is diluted with a carrier such as  $\alpha$ -alumina balls and then filled in the reaction tube to increase the heat-removing efficiency. When the heat conductivity of the catalyst layers in the reactor tube is insufficient, the heat of reaction is not removed and thus the temperature locally rises and the reaction temperature may not be suitably controlled so that the correct test may not be performed. The temperature of a hot spot set in the Catalyst b layer should be  $360 \pm 1^\circ\text{C}$ . In general, a temperature distribution is formed in the catalyst a layer and the catalyst b layer. Thus, the temperature in each catalyst layer is from 320 to  $360^\circ\text{C}$  during the reaction. When the reaction temperature is too high, the ruthenium compound, which is a catalytically active site, quickly agglomerates, and therefore F(b) may not be measured correctly. When the reaction temperature is too low, the ruthenium compound, which is a catalytically active site, slowly agglomerates, and thus F(b) may not be measured correctly. When the reaction is carried out by taking the above points into account, the test results can be obtained with good reproducibility.

In the case of the catalyst (3) of the first aspect of the present invention, the catalyst is obtained by main four preparation processes comprising the steps of:

supporting process, calcining process, hydrazine-treating process and oxidizing process. In addition to these four process, alkali metal chloride-adding process, washing process and drying process were added to the catalyst preparation process resulted in establishing the catalyst preparation process which has many processes. From the viewpoint of convenient preparation of catalysts, a process comprising the steps of: supporting process and drying process is very short catalyst preparation process which is comprised by two processes. The above process is preferred because the time of catalyst preparation is short and a preparation cost decrease. Moreover, the above catalysts were more active than the catalyst which was prepared by oxidizing the ruthenium catalyst prepared by hydrogenation of supported ruthenium chloride on a carrier by hydrogen.

The supported ruthenium oxide catalyst and the supported ruthenium chloride catalyst have a high catalytic activity.

The third aspect of the present invention relates to a process for producing chlorine by oxidizing hydrogen chloride with oxygen, which uses at least one catalyst selected from the group consisting of the following catalysts (1) to (6):

(1) a supported ruthenium oxide catalyst comprising titanium oxide which contains the rutile crystal form, and

which is obtained by calcination at a temperature of at least 550°C, as a carrier;

(2) a supported ruthenium oxide catalyst having a carbon monoxide adsorption amount of at least 87.5 ml per one gram of ruthenium contained in the catalyst, which is measured by the following steps of:

reducing 0.1 g of said catalyst at 220°C for 60 minutes with flowing a hydrogen gas at a flow rate of 50 ml/min. under atmospheric pressure, and

conducting a metal surface area measuring method according to a carbon monoxide pulse;

(3) a supported ruthenium oxide catalyst obtained by a preparation process comprising the steps of:

supporting a ruthenium compound on a carrier,

calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of hydrazine and an alkaline compound,

and

oxidizing said hydrazine-treated one;

(4) a supported ruthenium oxide catalyst produced by a process comprising the steps of:

supporting a ruthenium compound on a carrier,



and

calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, wherein, when the peak intensity ratio of the produced catalyst and that of the catalyst after a 50 hours reaction test, which are measured by an extended X-ray absorption fine structure analysis (EXAFS) method, are A(b) and B(b) respectively, the peak intensity ratios A(b) and B(b) satisfy the following equation (1):

$$1 \leq B(b)/A(b) \leq 1.45 \quad (1)$$

provided that  $A(b) \leq 0.8$ ,

wherein A(b) is a peak intensity ratio of as-produced Catalyst b measured by the EXAFS method, and B(b) is a peak intensity ratio of Catalyst b measured by the EXAFS method after the 50 hours reaction test; in which

50 Hours reaction test: Supported ruthenium oxide Catalysts a and b are filled in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and a hydrogen chloride gas is supplied under atmospheric pressure at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the reaction for 50 hours while maintaining the hot spot of

Catalyst b at  $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , in which Catalyst a is a supported ruthenium oxide catalyst having a chlorine formation activity per unit mass of the catalyst of  $2 \times 10^{-4}$  to  $3 \times 10^{-4}$  mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at  $300^{\circ}\text{C}$  with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide catalyst produced by the above process, and in which

EXAFS method: Catalyst b is measured by an X-ray absorption fine structure analysis (XAFS) method at the Ru-K absorption edge, and the peak intensity of the catalyst is evaluated by the peak around 0.32 nm in a radial distribution function obtained by the Fourier transformation of the EXAFS spectrum, wherein the peak intensity corresponds to the number of the second nearest neighbor ruthenium atoms of the X-ray absorbing ruthenium atoms in ruthenium dioxide, and the peak intensity ratio of the catalyst is calculated by dividing the peak intensity of the catalyst by that of ruthenium oxide having a particle size of at least 10 nm;

(5) a supported ruthenium oxide catalyst produced by a process comprising the following steps but not a treating step with hydrazine:

supporting a ruthenium compound on a titanium oxide

described in connection with the catalyst (2) of the first

aspect. The catalyst (3) used in the third aspect is described in connection with the catalyst (3) of the first aspect. The catalyst (4) used in the third aspect is described in connection with the catalyst (4) prepared by the process of the second aspect. The catalyst (5) used in the third aspect is described in connection with the catalyst (5) prepared by the process of the second aspect. The catalyst (6) used in the third aspect is described in connection with the catalyst (6) prepared by the process of the second aspect.

One preferable example of the catalyst (5) used in the process of third aspect of the present invention is a catalyst which is produced by a process comprising the following steps but not a treating step with hydrazine:

supporting a ruthenium compound on a carrier,  
and

calcining said supported one at a temperature of 200°C to 600°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, wherein the catalytic activity value of the produced catalyst and the catalytic activity value of the catalyst after 50 hours reaction test, which are measured by a catalytic activity test which is defined below, are respectively C(b) and D(b), and which satisfy the following equation (2):

$$0.79 \leq D(b)/C(b) \leq 1 \quad (2)$$

provided that  $C(b) \geq 3.0 \times 10^{-4}$  mol/min.g-cat.

wherein  $C(b)$  is a catalytic activity value of the produced catalyst b, which is measured by the catalytic activity

5 test and  $D(b)$  is a catalytic activity value of the catalyst b, which is measured by the catalytic activity test after a 50 hours reaction test;

in which

the 50 hours reaction test is carried out by filling  
10 supported ruthenium oxide Catalysts a and b in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and supplying, under atmospheric pressure, a hydrogen chloride gas at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an  
15 oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at  $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , wherein Catalyst a is a catalyst having a chlorine formation activity per unit mass of catalyst of  $2 \times 10^{-4}$  to  $3 \times 10^{-4}$  mol/min.g-cat.,  
20 which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at  $300^{\circ}\text{C}$  with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide Catalyst produced by the above process,  
25 and in which

Catalytic activity test: 2.3 to 2.5 grams of a catalyst is diluted by mixing with 10 to 20 g of a spherical  $\alpha$ -alumina carrier having a diameter of 2 mm, and filled in a quartz reactor tube having an inner diameter of 12 mm, then a hydrogen chloride gas and an oxygen gas are supplied in the reactor under atmospheric pressure at flow rates of 190 to 210 ml/min. and 190 to 210 ml/min., respectively (both volumes being converted to those at 0°C under 101 kPa) while heating the reactor in an electric furnace and maintaining the internal temperature (hot spot) at  $300 \pm 1^\circ\text{C}$ , after  $2.0 \pm 1.0$  hours from the start of the reaction, an exit gas from the reactor is sampled by passing it through a 30 mass % aqueous solution of potassium iodide, the amount of formed chlorine and the amount of unreacted hydrogen chloride are measured by an iodine titration method and a neutralization titration method, respectively, and thereafter a chlorine formation activity per unit mass of the catalyst is calculated by the following equation and used as a catalyst activity:

Chlorine formation activity per unit mass of the catalyst (mol/min.g-cat.) =  
Amount of chlorine gas from reactor exit (mol/min.) /  
catalyst weight (g).

The preferable example of the catalyst (5) used in the process of the third aspect of the present invention is

already explained in connection with the preferable example of the catalyst (5) prepared by the process of the second aspect of the present invention.

One preferable example of the catalyst (6) used in the process of third aspect of the present invention is a catalyst which is produced by a process comprising the following steps but neither a calcining step nor a treating step with hydrazine:

supporting a ruthenium halide on a titanium oxide carrier containing the rutile crystal form, and

drying said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere at a temperature of 20°C to less than 200°C, wherein the catalytic activity value of the produced catalyst and the catalytic activity value of the catalyst after 50 hours reaction test, which are measured by a catalytic activity test which is defined below, are respectively E(b) and F(b), and which satisfy the following equation (3):

$$0.80 \leq F(b)/E(b) \leq 1.20 \quad (3)$$

provided that  $E(b) \geq 3.0 \times 10^{-4}$  mol/min.g-cat.

in which

50 Hours reaction test: Supported ruthenium oxide

Catalysts a and b are filled in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and a hydrogen chloride gas is supplied under atmospheric pressure at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at  $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , in which Catalyst a is a supported ruthenium oxide catalyst having a chlorine formation activity per unit mass of the catalyst of  $2 \times 10^{-4}$  to  $3 \times 10^{-4}$  mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at  $300^{\circ}\text{C}$  with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide catalyst produced by the above process, and in which

Catalytic activity test: 2.3 to 2.5 grams of a catalyst is diluted by mixing with 10 to 20 g of a spherical  $\alpha$ -alumina carrier having a diameter of 2 mm, and filled in a quartz reactor tube having an inner diameter of 12 mm, then a hydrogen chloride gas and an oxygen gas are supplied in the reactor under atmospheric pressure at flow rates of 190 to 210 ml/min. and 190 to 210 ml/min., respectively (both volumes being converted to those at  $0^{\circ}\text{C}$  under 101 kPa) while heating the reactor in an electric



furnace and maintaining the internal temperature (hot spot) at  $300 \pm 1^\circ\text{C}$ , after  $2.0 \pm 1.0$  hours from the start of the reaction, an exit gas from the reactor is sampled by passing it through a 30 mass % aqueous solution of potassium iodide, the amount of formed chlorine and the amount of unreacted hydrogen chloride are measured by an iodine titration method and a neutralization titration method, respectively, and thereafter a chlorine formation activity per unit mass of the catalyst is calculated by the following equation and used as a catalyst activity:

Chlorine formation activity per unit mass of the catalyst  
(mol/min.g-cat.) =  
Amount of chlorine gas from reactor exit (mol/min.) /  
catalyst weight (g).

The preferable example of the catalyst (6) used in the process of the third aspect of the present invention is already explained in connection with the preferable example of the catalyst (6) prepared by the process of the second aspect of the present invention.

The process of the third aspect of the present invention produces chlorine by oxidizing hydrogen chloride with oxygen in the presence of one or more of the above catalysts (1) to (6). In this process, the reaction system includes, for example, a flow system such as a fixed bed system or a fluidized bed system. Preferably, a gas phase

fixed bed flow system and a gas phase fluidized bed flow system are used. The fixed bed system has an advantage that no separation of the reaction gas from the catalyst is required and that a high conversion can be accomplished because the raw gas can be sufficiently contacted with the catalyst. The fluidized bed system has an advantage that heat in the reactor can be sufficiently removed and the temperature distribution range in the reactor can be minimized.

When the reaction temperature is high, ruthenium oxide in a highly oxidized state may be volatilized. Thus, the oxidation reaction is preferably conducted at a relatively low temperature, preferably, at a temperature of from 100 to 500°C, more preferably from 200 to 380°C.

The reaction pressure is usually from atmospheric pressure to about 5.07 MPa.

As a source of oxygen gas, an air as such or pure oxygen may be used. Since other components may be discharged out of the plant at the same time as the discharge of inert nitrogen gas, pure oxygen is containing no inert gas is preferably used.

A theoretical molar amount of oxygen based on hydrogen chloride is 1/4 mole, but oxygen is usually fed in an amount of 0.1 to 10 times larger than the theoretical amount.

In the case of the fixed bed gas phase flow system, the amount of the catalyst is usually from about 10 to 20,000 hr<sup>-1</sup> in terms of a ratio (GHSV) to a feed rate of hydrogen chloride as the raw material under atmospheric pressure. GHSV means a Gas Hourly Space Velocity, which is a ratio of a volume of fed hydrogen chloride (liter/hr.) to a volume of the catalyst (liters).

#### Example 1

A catalyst was prepared as follows.

To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (50.0 g), pure water (35.3 g) and titanium oxide sol (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (6.6 g) were added and kneaded.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 2 hours to obtain white noodle-form titanium oxide (49.1 g).

The above operation was repeated, and white noodle-form titanium oxide (105.0 g in total) was obtained.

The obtained titanium oxide solid was heated under air from room temperature to 700°C over 2 hours and calcined at the same temperature (700°C) for 3 hours to obtain white noodle-form titanium oxide (102.3 g).

After calcination, the noodle-form solid was cut to a

length of about 5 mm to obtain an extruded white titanium oxide carrier.

Then, the carrier (100.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 37.3 mass %) (12.75 g) dissolved in pure water (42.5 g), and dried at 60°C for 2 hours.

Then, 21.6g of this solid from the obtained one was heated under air from room temperature to 200°C over 1 hour and calcined at the same temperature for 2 hours.

The calcined solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (13.3 g), pure water (120 g) and hydrazine monohydrate (3.20 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 155 minutes, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated eight times. The pH of the first wash liquid was 11.4, and that of the eighth wash liquid was 7.4.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the black solid.

Then, the black solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same  
5 temperature for 3 hours to obtain the black solid (20.9 g).

After calcination, pure water (500 ml) was added to the black solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation was repeated six times. Thereafter, an aqueous solution of  
10 silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded black ruthenium oxide catalyst supported on titanium oxide (20.6 g).

15 The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 5.9 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 4.5 \text{ mass \%}$$

20 Next, the adsorbed amount of carbon monoxide was measured by metal surface area measuring method (MSA).

The catalyst (0.1 g) was sampled and the adsorbed amount of carbon monoxide was measured under the following conditions:

25 -Apparatus: Full automatic apparatus for measuring gas

adsorption on catalysts R 6015 (manufactured by OKURA  
RIKEN)

-Hydrogen flow rate: 50 ml/min.

-Heating rate: 20°C/min.

5 -Reducing conditions: 220°C, 60 minutes

-Helium purging: He 50 ml/min, 5 minutes

-Cooling rate: 25°C/min.

-Carbon monoxide adsorption: Carbon monoxide being adsorbed  
on the catalyst by pulse injecting carbon monoxide (each  
10 0.45 ml) several times at 50°C with flowing helium at 50  
ml/min.

The measurement was carried out twice. The averaged  
adsorbed amount of carbon monoxide was 4.42 ml/g-cat., and  
the adsorbed amount per unit mass of ruthenium was 98.2  
15 ml/g-Ru.

The obtained ruthenium oxide catalyst supported on  
titanium oxide (2.5 g) was diluted by mixing with a  
commercially available spherical  $\alpha$ -alumina carrier having a  
diameter of 2 mm (SSA 995 manufactured by NIKKATO Co.,  
20 Ltd.) (10 g) to dilute the catalyst, and then charged in a  
quartz reactor tube having an inner diameter of 12 mm. To  
the reactor tube, hydrogen chloride gas and oxygen gas were  
supplied at flow rates of 192 ml/min. and 192 ml/min.,  
respectively (each converted to a volume at 0°C under 1  
25 atm.)

25 When 2.4 hours after the start of the reaction, the





g) dissolved in pure water (8.5 g), dried at room temperature overnight, and further dried at 60°C for 2 hours.

The obtained solid (22.4 g) was heated under air from room temperature to 300°C over 1.5 hours while supplying an air at a flow rate of 200 ml/min. and calcined at the same temperature for 2 hours.

The calcined solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (13.2 g), pure water (120 g) and hydrazine monohydrate (3.20 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 155 minutes, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated seven times. The pH of the first wash liquid was 10.5, and that of the seventh wash liquid was 8.0.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the black solid.

Then, the black solid was heated under air from room

temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the black solid (21.3 g).

After calcination, pure water (500 ml) was added to the black solid and the mixture was stirred, followed by  
 5 recovering of the solid by filtration. The same operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to  
 10 obtain an extruded black ruthenium oxide catalyst supported on titanium oxide (21.1 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 5.9 \text{ mass \%}$$

15 The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 4.5 \text{ mass \%}$$

The obtained ruthenium oxide catalyst supported on titanium oxide (1.0 g) was diluted by mixing with a commercially available spherical  $\alpha$ -alumina carrier having a  
 20 diameter of 2 mm (20 g) to dilute the catalyst, and charged in the quartz reactor tube. Then, the reaction was carried out in the same manner as that in Example 1 except that the oxygen was supplied at a flow rate of 206 ml/min.

When 2.0 hours after the start of the reaction, the  
 25 chlorine formation activity per unit mass of the catalyst

was  $22.8 \times 10^{-4}$  mol/min.g-cat.

### Example 4

A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal)  
5 manufactured by Sakai Chemical Industry Co., Ltd.) (30.0 g)  
and aluminum oxide powder (AES-12 manufactured by Sumitomo  
Chemical Co., Ltd.) (30.0 g) were thoroughly mixed. To the  
mixture, pure water (19.0 g) and titanium oxide sol (CSB  
(TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical  
10 Industry Co., Ltd.) (7.9 g) were added and kneaded. To the  
kneaded mixture, pure water (0.6 g) was added and further  
kneaded until an adequate viscosity was reached.

This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 2 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina.

The obtained white noodle-form titanium oxide- $\alpha$ -alumina was heated under air from room temperature to 600°C over 1.7 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina (50.8 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- $\alpha$ -alumina carrier.

25 Then, the carrier (20.0 g) was impregnated with an

aqueous solution of commercially available ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 38.2 mass %) (1.63 g) dissolved in pure water (6.1 g), dried at room temperature overnight and further dried at 60°C for 2 hours.

5           The obtained solid was heated under air from room temperature to 250°C over 1.25 hours and calcined at the same temperature for 2 hours.

The calcined solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (8.5 g), pure water (120 g) and hydrazine monohydrate (2.05 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated seven times. The pH of the first wash liquid was 10.9, and that of the seventh wash liquid was 7.2.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the black solid.

Then, the black solid was heated under air from room  
25 temperature to 350°C over 1 hour and calcined at the same

temperature for 3 hours to obtain the black solid.

After calcination, pure water (500 ml) was added to the black solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation  
5 was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded black ruthenium oxide catalyst supported  
10 on titanium oxide- $\alpha$ -alumina (20.7 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.9 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

15 
$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.0 \text{ mass } \%$$

The obtained ruthenium oxide catalyst supported on titanium oxide- $\alpha$ -alumina (2.5 g) was charged in the quartz reactor tube, and the reaction was carried out in the same manner as that in Example 1 except that the internal  
20 temperature (hot spot) was 301°C.

When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $9.1 \times 10^{-4} \text{ mol/min.g-cat.}$

#### Example 5

25 A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (20.0 g) and aluminum oxide powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (20.0 g) were thoroughly mixed. To the  
5 mixture, pure water (14.6 g) and titanium oxide sol (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (5.26 g) were added and kneaded, and further kneaded until an adequate viscosity was reached.

This mixture was molded by extrusion in the form of  
10 noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina.

The obtained white noodle-form solid was heated under air from room temperature to 600°C over 1.7 hours and  
15 calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina (33.0 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- $\alpha$ -alumina carrier.

20 Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride (RuCl<sub>3</sub>.nH<sub>2</sub>O, ruthenium content: 38.2 mass %) (1.63 g) dissolved in pure water (5.9 g), dried at room temperature overnight and further dried at 60°C for 2 hours.

25 The obtained solid was heated from room temperature to

200°C over 1 hour while supplying an air at a flow rate of 200 ml/min. and calcined at the same temperature for 2 hours.

The calcined solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (8.5 g), pure water (120 g) and hydrazine monohydrate (2.05 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 10.4, and that of the fifth wash liquid was 7.4.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the black solid (20.8 g).

Then, the black solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the black solid.

After calcination, pure water (500 ml) was added to the black solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation

was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to  
5 obtain an extruded black ruthenium oxide catalyst supported on titanium oxide- $\alpha$ -alumina (20.5 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \text{Al}_2\text{O}_3)] \times 100 = 3.9 \text{ mass \%}$$

10 The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.0 \text{ mass \%}$$

Next, the adsorbed amount of carbon monoxide was measured by MSA under the same conditions as those in Example 1. The measurement was carried out twice. The  
15 averaged adsorbed amount of carbon monoxide was 2.98 ml/g-cat., and the adsorbed amount per unit mass of ruthenium was 99.3 ml/g-Ru.

The obtained ruthenium oxide catalyst supported on titanium oxide- $\alpha$ -alumina (2.5 g) was charged in the quartz  
20 reactor tube and the reaction was carried out in the same manners as those in Example 1 except that the oxygen gas was supplied under atmospheric pressure at a flow rate of 206 ml/l.

When 2.0 hours after the start of the reaction, the  
25 chlorine formation activity per unit mass of the catalyst



was  $9.1 \times 10^{-4}$  mol/min.g-cat.

#### Example 6

A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal)  
5 manufactured by Sakai Chemical Industry Co., Ltd.) (30.1 g)  
and aluminum oxide powder (AES-12 manufactured by Sumitomo  
Chemical Co., Ltd.) (60.0 g) were thoroughly mixed. To the  
mixture, pure water (20.3 g) and titanium oxide sol (CSB  
(TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical  
10 Industry Co., Ltd.) (11.9 g) were added and kneaded, and  
further kneaded until an adequate viscosity was reached.

This mixture was molded by extrusion in the form of  
noodles having a diameter of 1.5 mm $\phi$ , and dried under air  
at 60°C for 4 hours to obtain white noodle-form titanium  
15 oxide- $\alpha$ -alumina.

Then, 55.5g of this solid from the obtained white  
noodle-form one was heated under air from room temperature  
to 600°C over 1.7 hours and calcined at the same  
temperature for 3 hours to obtain white noodle-form  
20 titanium oxide- $\alpha$ -alumina (53.8 g).

After calcination, the noodle-form solid was cut to a  
length of about 5 mm to obtain an extruded white titanium  
oxide- $\alpha$ -alumina carrier.

Then, the carrier (20.0 g) was impregnated with an  
25 aqueous solution of commercially available ruthenium

chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 38.2 mass %) (0.82 g) dissolved in pure water (4.49 g), dried at room temperature overnight and further dried at 60°C for 2 hours.

The obtained solid was heated from room temperature to 200°C over 1 hour while supplying an air at a flow rate of 200 ml/min. and calcined at the same temperature for 2 hours.

The calcined solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (4.2 g), pure water (120 g) and hydrazine monohydrate (1.03 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 10.6, and that of the fifth wash liquid was 7.3.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the black solid.

Then, the black solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same

temperature for 3 hours to obtain the black solid.

After calcination, pure water (500 ml) was added to the black solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation  
5 was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded black ruthenium oxide catalyst supported  
10 on titanium oxide- $\alpha$ -alumina (20.2 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.0 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

15 
$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.53 \text{ mass } \%$$

Next, the adsorbed amount of carbon monoxide was measured by MSA under the same conditions as those in Example 1. The measurement was carried out twice. The averaged adsorbed amount of carbon monoxide was 1.73 ml/g-  
20 cat., and the adsorbed amount per unit mass of ruthenium was 113.1 ml/g-Ru.

The obtained ruthenium oxide catalyst supported on titanium oxide- $\alpha$ -alumina (2.5 g) was charged in the quartz reactor tube and the reaction was carried out in the same  
25 manners as those in Example 1.

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide carrier.

Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 37.3 mass %) (2.55 g) dissolved in pure water (7.6 g), and dried at 60°C for 2 hours.

The obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (13.2 g), pure water (120 g) and hydrazine monohydrate (3.20 g). Bubbling was observed as soon as the solid was dipped in the solution. After 60 minutes, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 9.0, and that of the fifth wash liquid was 6.0.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the black solid.

Then, the black solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the black solid (21.2 g).

After calcination, pure water (500 ml) was added to

the black solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to  
5 confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded black ruthenium oxide catalyst supported on titanium oxide (20.4 g).

The calculated content of ruthenium oxide was as  
10 follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 5.9 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 4.5 \text{ mass } \%$$

Next, the adsorbed amount of carbon monoxide was  
15 measured by MSA under the same conditions as those in Example 1. The measurement was carried out twice. The averaged adsorbed amount of carbon monoxide was 3.28 ml/g-cat., and the adsorbed amount per unit mass of ruthenium was 72.9 ml/g-Ru.

## 20 Example 8

A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (40.1 g) and  $\alpha$ -alumina powder (AES-12 manufactured by Sumitomo  
25 Chemical Co., Ltd.) (40.0 g) were thoroughly mixed. To the

mixture, the mixed solution of titanium oxide sol (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (10.6 g) and pure water (31.0 g) was added and kneaded.

5 This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina.

10 The obtained white noodle-form titanium oxide- $\alpha$ -alumina was heated under air from room temperature to 600°C over 1.6 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina (75.4 g).

15 After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- $\alpha$ -alumina carrier. The same carrier was prepared by the same method as above, and two portions of the prepared carrier were combined.

20 Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride (RuCl<sub>3</sub>.nH<sub>2</sub>O, ruthenium content: 37.3 mass %) (1.62 g) dissolved in pure water (5.86 g) and dried at 60°C for 2 hours.

25 The obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (8.38 g), pure

water (40 g) and hydrazine monohydrate (2.04 g). Bubbling  
was observed as soon as the calcined solid was dipped in  
the solution. After 1 hour, the supernatant was removed by  
filtration. Then, pure water (500 ml) was added to the  
5 recovered solid and the solid was washed for 30 minutes,  
followed by filtration. The washing and filtration were  
repeated five times. The pH of the first wash liquid was  
9.7, and that of the fifth wash liquid was 7.0.

To the filtrated solid, a 0.5 mol/l aqueous solution  
10 of potassium chloride (50 g) was added, and stirred,  
followed by recovering of the solid by filtration. The  
same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to  
obtain the gray solid. Furthermore, another two portions  
15 of the gray solid were produced by the same method, and  
three portions were combined.

Then, the gray solid was heated under air from room  
temperature to 350°C over 1 hour and calcined at the same  
temperature for 3 hours to obtain the bluish gray solid.  
20 The bluish gray solid was prepared by the same method as  
above, and two portions of the prepared solid were combined.

After calcination, pure water (500 ml) was added to  
the black solid and the mixture was stirred, followed by  
recovering of the solid by filtration. The same operation  
25 was repeated five times. Thereafter, an aqueous solution



of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded bluish gray ruthenium oxide catalyst  
5 supported on titanium oxide- $\alpha$ -alumina (124.6 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.8 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

10 
$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.9 \text{ mass \%}$$

The adsorbed amount of carbon monoxide was measured by MSA under the same conditions as those in Example 1. The measurement was carried out twice. The averaged adsorbed amount of carbon monoxide was 2.36 ml/g-cat., and the  
15 adsorbed amount per unit mass of ruthenium was 81.4 ml/g-Ru.

#### Example 9

A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (30.0 g)  
20 and  $\alpha$ -alumina powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (30.0 g) were thoroughly mixed. To the mixture, the mixed solution of titanium oxide sol (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) and pure water (22.0 g) was  
25 added and kneaded.

This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina (53.1 g).

5 The obtained white noodle-form titanium oxide- $\alpha$ -alumina was heated under air from room temperature to 800°C over 2.2 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina (52.3 g).

10 After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- $\alpha$ -alumina carrier.

Then, the carrier (25.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride (RuCl<sub>3</sub>.nH<sub>2</sub>O, ruthenium content: 37.3 mass %) (1.01 g) dissolved in pure water (6.9 g) and dried at 60°C for 2 hours.

The obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (5.24 g), pure water (150 g) and hydrazine monohydrate (1.26 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were

20

25

repeated five times. The pH of the first wash liquid was 9.1, and that of the fifth wash liquid was 6.7.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred,  
5 followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the gray solid..

Then, the gray solid was heated under air from room  
10 temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the bluish gray solid.

After calcination, pure water (500 ml) was added to the black solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation  
15 was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded bluish gray ruthenium oxide catalyst  
20 supported on titanium oxide- $\alpha$ -alumina (24.8 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \text{Al}_2\text{O}_3)] \times 100 = 1.9 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

25 
$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.5 \text{ mass } \%$$

25 After calcination, the noodle-form solid was cut to a

length of about 5 mm to obtain an extruded white titanium oxide carrier.

Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 37.3 mass %) (1.61 g) dissolved in pure water (10.2 g), and dried at 60°C for 2 hours.

The obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (8.34 g), pure water (121 g) and hydrazine monohydrate (2.02 g). Bubbling was observed as soon as the dried solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 8.9, and that of the fifth wash liquid was 5.7.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the gray solid.

Then, the gray solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same

temperature for 3 hours to obtain the bluish gray solid.

After calcination, pure water (500 ml) was added to the bluish gray solid and the mixture was stirred, followed by recovering of the solid by filtration. The same  
5 operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded bluish gray ruthenium oxide catalyst  
10 supported on titanium oxide (20.6 g).

A packing density of the obtained catalyst was measured by packing the catalyst in a 50 ml graduated cylinder, and calculated from a packing weight and a packing volume according to the following equation:

15 
$$\text{Packing density} = \text{Packing weight} / \text{Packing volume}$$

The packing density was 0.91 g/ml.

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 3.8 \text{ mass \%}$$

20 The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 2.9 \text{ mass \%}$$

The obtained catalyst is named "Catalyst c".

2) The second catalyst of this Example was prepared as follows.

25 Titanium oxide powder (STR-60R (100 % rutile crystal)

manufactured by Sakai Chemical Industry Co., Ltd.) (30.0 g)  
and  $\alpha$ -alumina powder (AES-12 manufactured by Sumitomo  
Chemical Co., Ltd.) (30.0 g) were thoroughly mixed. To the  
mixture, titanium oxide sol (CSB ( $\text{TiO}_2$  content: 38 mass %)  
5 manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g)  
and pure water (22.0 g) were added and kneaded.

This mixture was molded by extrusion in the form of  
noodles having a diameter of 1.5 mm $\phi$ , and dried under air  
at 60°C for 4 hours to obtain white noodle-form titanium  
oxide- $\alpha$ -alumina (53.1 g).  
10

The obtained white noodle-form titanium oxide- $\alpha$ -  
alumina was heated under air from room temperature to 800°C  
over 2.2 hours and calcined at the same temperature for 3  
hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina  
15 (52.3 g).

After calcination, the noodle-form solid was cut to a  
length of about 5 mm to obtain an extruded white titanium  
oxide- $\alpha$ -alumina carrier.

Then, the carrier (25.0 g) was impregnated with an  
aqueous solution of commercially available ruthenium  
20 chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 37.3 mass %) (1.01  
g) dissolved in pure water (6.9 g) and dried at 60°C for 2  
hours.

The obtained solid was dipped in a solution containing  
25 2N aqueous solution of potassium hydroxide (5.24 g), pure

water (150 g) and hydrazine monohydrate (1.26 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 9.1, and that of the fifth wash liquid was 6.7.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the gray solid.

Then, the gray solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the bluish gray solid (24.8 g).

After calcination, pure water (500 ml) was added to the bluish gray solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to



obtain an extruded bluish gray ruthenium oxide catalyst supported on titanium oxide- $\alpha$ -alumina (20.6 g). The packing density of this catalyst was 1.02 g/ml.

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.9 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.4 \text{ mass \%}$$

The obtained catalyst was named "Catalyst b".

3) The third catalyst of this Example was prepared as follows.

A commercially available  $\alpha$ -alumina (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (30.1 g), ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 37.3 mass %) (1.62 g), pure water (3.0 g) and alumina sol (ALUMINA SOL 200 manufactured by Nissan Chemical Industries, Ltd.) (8.53 g) were thoroughly mixed. A dry air was blown onto the mixture at room temperature to dry the mixture until an adequate viscosity was reached.

This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 4 hours to obtain brown noodle-form ruthenium oxide- $\alpha$ -alumina.

The obtained brown noodle-form ruthenium oxide- $\alpha$ -alumina was heated under air from room temperature to 350°C

over 1 hour and calcined at the same temperature for 3 hours to obtain gray noodle-form ruthenium oxide catalyst supported on  $\alpha$ -alumina (25.8 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.5 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.9 \text{ mass } \%$$

The packing density of obtained catalyst was 1.31 g/ml.

The catalyst obtained by the same preparation method which was mentioned above was named "Catalyst a".

4) In a glass test reactor tube having an inner diameter of 15 mm, in which a thermocouple-protective tube having an outer diameter of 6 mm was inserted, above-prepared Catalysts a, b and c were charged in a volume ratio of 2:13:5 (a:b:c) in a reactor in this order from the inlet of a reactor. Each Catalyst had been diluted with the same volume ratio of  $\alpha$ -alumina spheres having a diameter of 2 mm (SSA 995 manufactured by NIKKATO). The charged volumes of Catalysts a, b and c were as follows:

Catalyst a: 0.68 ml (0.89 g)

Catalyst b: 4.33 ml (4.42 g)

Catalyst c: 1.69 ml (1.54 g)

The total volume of charged catalysts was 6.7 ml.

The upper zone of the Catalyst layer was formed by the

Catalyst a and the Catalyst b, while the lower zone of the Catalyst layer was formed by the Catalyst c, and each zone was heated in a respective electric furnace.

Hydrogen chloride gas and oxygen gas were supplied and  
5 flowed under atmospheric pressure from the upper zone to the lower zone at flow rates of 50 ml/min. and 25 ml/min., respectively (each converted to a volume at 0°C under 101 kPa.) This reaction operation was carried out for 80 hours under the above conditions while maintaining the conversion  
10 of hydrogen chloride at higher than 70 %. After 80 hours, the internal temperature (hot spot) of the upper zone in the test reactor tube was 343°C, while that of the lower zone was 297°C. At this time, the gas from the outlet of the test reactor tube was sampled by passing it through an  
15 aqueous 30 mass % potassium iodide solution, and the amount of chlorine formed and the amount of unreacted hydrogen chloride were determined by iodometric titration and neutralization titration, respectively. The conversion of hydrogen chloride was 91.2 %.

20 5) Furthermore, the activity of Catalyst c was measured as follows:

The activity of Catalyst c was represented by  $M(c)$ .

Catalyst c was isolated from the mixture of Catalyst c and the  $\alpha$ -alumina carrier used in the step 4), and one gram  
25 of Catalyst c was thoroughly mixed again with the

commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (4 g) to dilute Catalyst c, and diluted Catalyst c was charged in a quartz reactor tube having an inner diameter of 12 mm.

5 Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 77 ml/min. and 77 ml/min., respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the  
10 internal temperature (hot spot) at 299°C. When 2.2 hours after the start of the reaction, the gas from the outlet of the reactor tube was sampled by passing it through an aqueous 30 mass % potassium iodide solution, and the amount of chlorine formed and the amount of unreacted hydrogen  
15 chloride were determined by iodometric titration and neutralization titration, respectively.

The chlorine formation activity per unit mass of the catalyst, which was calculated according to the following equation, was  $8.6 \times 10^{-4}$  mol/min.g-cat.:

20 Chlorine formation activity per unit mass of the catalyst(mol/min.g-cat.) =  
Amount of outlet chlorine formed per unit time (mol/min.)/  
weight of catalyst (g)

6) In this step, the same Catalysts a and c as those  
25 used in the step 4) were used. As Catalyst b, one prepared

by the same method as that of the step 2) was used.

In a nickel test reactor tube having an inner diameter of 14 mm, in which a thermocouple-protective tube having an outer diameter of 5 mm was inserted, Catalysts a, b and c were charged in a volume ratio of 2:13:5 (a:b:c) from the inlet of a reactor. Each Catalyst had been diluted with the same volume ratio of  $\alpha$ -alumina spheres having a diameter of 2 mm (SSA 995 manufactured by NIKKATO). The charged volumes of Catalysts a, b and c were as follows:

10 Catalyst a: 1.73 ml (2.27 g)

Catalyst b: 11.13 ml (11.35 g)

Catalyst c: 4.33 ml (3.94 g)

The total volume of charged catalysts was 17.2 ml.

The upper zone of the Catalyst layer was formed by the Catalyst a and the Catalyst b, while the lower zone of the Catalyst layer was formed by the Catalyst c, and each zone was heated in a respective electric furnace.

Hydrogen chloride gas and oxygen gas were supplied and flowed under atmospheric pressure from the upper zone to the lower zone at flow rates of 130 ml/min. and 65 ml/min., respectively (each converted to a volume at 0°C under 101 kPa.) This reaction operation was carried out for 512 hours under the same conditions while maintaining the conversion of hydrogen chloride at higher than 70 %. After 512 hours, the internal temperature (hot spot) of the upper

zone in the test reactor tube was 352°C, while that of the lower zone was 301°C. At this time, the conversion of hydrogen chloride was 91.1 %.

7) Furthermore, the activity of Catalyst c was  
5 measured as follows:

This activity of Catalyst c was represented by  $N(c)$ .

Catalyst c was isolated from the mixture of Catalyst c and the  $\alpha$ -alumina carrier used in the step 6), and 2.5 grams of Catalyst c was thoroughly mixed again with the commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (10 g) to dilute Catalyst c, and diluted Catalyst c was charged in a quartz reactor tube having an inner diameter of 12 mm. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. and 192 ml/min., respectively. The quartz reactor tube was heated with an electric furnace to keep the internal temperature (hot spot) at 300°C. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $7.6 \times 10^{-4}$  mol/min.g-cat.

Accordingly, the ratio of N(c) to M(c)  $[N(c)/M(c)]$  was 0.89.

From the above result, it can be seen that Catalyst c  
25 had the high catalytic activity, and could produce chlorine

with a smaller amount of the catalyst at a lower temperature. Furthermore, when Catalyst c was used in the above chlorine formation reaction, it had a longer life.

#### Example 11

5           1) The first catalyst of this Example was prepared as follows.

To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (80.0 g), pure water (64.2 g) and titanium oxide sol (CSB  
10 (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (10.6 g) were added and kneaded. A dry air was blown onto the kneaded mixture at room temperature to dry the mixture until an adequate viscosity was reached.

The mixture was molded by extrusion in the form of  
15 noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide.

The obtained titanium oxide solid was heated under air from room temperature to 800°C over 2.2 hours and calcined  
20 at the same temperature for 3 hours to obtain white noodle-form titanium oxide (72.1 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide carrier.

25           Then, the carrier (20.0 g) was impregnated with an

aqueous solution of commercially available ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 37.3 mass %) (2.04 g) dissolved in pure water (8.18 g), and dried at 60°C for 2 hours.

5           The obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (10.6 g), pure water (120 g) and hydrazine monohydrate (2.55 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by  
10       filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 9.7, and that of the fifth wash liquid was 5.9.

15           Another two portions of the same solid were prepared by the same method as above, and three portions of the solid were combined.

          To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (150 g) was added, and stirred,  
20       followed by recovering of the solid by filtration. The same operation was repeated three times.

          The obtained solid was dried at 60°C for 4 hours to obtain the gray solid.

          Then, the gray solid was heated under air from room  
25       temperature to 350°C over 1 hour and calcined at the same



temperature for 3 hours to obtain the bluish gray solid.

After calcination, pure water (500 ml) was added to the bluish gray solid and the mixture was stirred, followed by recovering of the solid by filtration. The same  
5 operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded bluish gray ruthenium oxide catalyst  
10 supported on titanium oxide (61.6 g).

A packing density of the obtained catalyst was measured and calculated in the same manner as that of Example 10. The packing density was 0.83 g/ml.

The calculated content of ruthenium oxide was as  
15 follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 4.8 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 3.6 \text{ mass } \%$$

The obtained catalyst is named "Catalyst d".

20 2) The second catalyst of this Example was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (64.0 g) and  $\alpha$ -alumina powder (AES-12 manufactured by Sumitomo  
25 Chemical Co., Ltd.) (16.0 g) were thoroughly mixed. To the

mixture, titanium oxide sol (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (10.6 g) and pure water (49.3 g) were added and kneaded.

This mixture was molded by extrusion in the form of  
5 noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina.

The obtained white noodle-form titanium oxide- $\alpha$ -alumina was heated under air from room temperature to 600°C  
10 over 1.6 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina (73.9 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium  
15 oxide- $\alpha$ -alumina carrier.

Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride (RuCl<sub>3</sub>.nH<sub>2</sub>O, ruthenium content: 37.3 mass %) (2.03 g) dissolved in pure water (7.9 g) and dried at 60°C for 2  
20 hours.

The obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (10.5 g), pure water (120 g) and hydrazine monohydrate (2.55 g). Bubbling was observed as soon as the calcined solid was dipped in  
25 the solution. After 1 hour, the supernatant was removed by

filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 9.2, and that of the fifth wash liquid was 5.8. Another two portions of the same solid were prepared by the same method as above, and three portions of the solid were combined.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the gray solid (62.4 g).

Then, the gray solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the bluish gray solid (61.5 g).

After calcination, pure water (500 ml) was added to the bluish gray solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to

obtain an extruded bluish gray ruthenium oxide catalyst supported on titanium oxide- $\alpha$ -alumina (60.6 g). The packing density of this catalyst was 0.89.

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 4.8 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.6 \text{ mass \%}$$

The obtained catalyst was named "Catalyst c".

3) The third catalyst of this Example was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (40.1 g) and  $\alpha$ -alumina powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (40.0 g) were thoroughly mixed. To the mixture, the mixed solution of titanium oxide sol (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (10.6 g) and pure water (31.0 g) was added and kneaded.

This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina.

The obtained white noodle-form titanium oxide- $\alpha$ -alumina was heated under air from room temperature to 600°C

over 1.6 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina (75.4 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- $\alpha$ -alumina carrier. The same carrier was prepared by the same method as above, and two portions of the prepared carrier were combined.

Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 37.3 mass %) (1.62 g) dissolved in pure water (5.86 g) and dried at 60°C for 2 hours.

The obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (8.38 g), pure water (40 g) and hydrazine monohydrate (2.04 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 9.7, and that of the fifth wash liquid was 7.0.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred,

followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the gray solid. Furthermore, another two portions  
5 of the gray solid were produced by the same method, and three portions were combined.

Then, the gray solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the bluish gray solid.  
10 The bluish gray solid was prepared by the same method as above, and two portions of the prepared solid were combined.

After calcination, pure water (500 ml) was added to the bluish gray solid and the mixture was stirred, followed by recovering of the solid by filtration. The same  
15 operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded bluish gray ruthenium oxide catalyst  
20 supported on titanium oxide- $\alpha$ -alumina (124.6 g). The packing density of this catalyst was 1.02 g/ml.

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.8 \text{ mass \%}$$

25 The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.9 \text{ mass \%}$$

The obtained catalysy is named "Catalyst b".

4) The fourth catalyst of this Example was prepared as follows.

5        A commercially available  $\alpha$ -alumina (AES-12  
manufactured by Sumitomo Chemical Co., Ltd.) (30.1 g),  
ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 37.3  
mass %) (1.62 g), pure water (3.0 g) and alumina sol  
(ALUMINA SOL 200 manufactured by Nissan Chemical Industries,  
10    Ltd.) (8.53 g) were thoroughly mixed. A dry air was blown  
onto the mixture at room temperature to dry the mixture  
until an adequate viscosity was reached.

      This mixture was molded by extrusion in the form of  
noodles having a diameter of 1.5 mm $\phi$ , and dried under air  
15    at 60°C for 4 hours to obtain brown noodle-form ruthenium  
oxide- $\alpha$ -alumina.

      The obtained brown noodle-form ruthenium oxide- $\alpha$ -  
alumina was heated under air from room temperature to 350°C  
over 1 hour and calcined at the same temperature for 3  
20    hours to obtain gray noodle-form ruthenium oxide catalyst  
supported on  $\alpha$ -alumina (25.8 g).

      The calculated content of ruthenium oxide was as  
follows:

$$[\text{RuO}_2/(\text{RuO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.5 \text{ mass \%}$$

25        The calculated content of ruthenium was as follows:

Hydrogen chloride gas and oxygen gas were supplied and flowed under atmospheric pressure from the upper zone to the lower zone at flow rates of 130 ml/min. and 65 ml/min.,



Catalyst d (2.5 g) was diluted by mixing with the commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (10 g), and diluted Catalyst d was charged in a quartz reactor tube having an inner diameter of 12 mm. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. and 192 ml/min., respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the internal temperature (hot

spot) at 300°C. When 2.0 hours after the start of the reaction, the gas from the outlet of the reactor tube was sampled by passing it through an aqueous 30 mass % potassium iodide solution, and the amount of chlorine  
5 formed and the amount of unreacted hydrogen chloride were determined by iodometric titration and neutralization titration, respectively.

After the following time period from the start of the reaction, a portion of Catalyst d was removed from the  
10 reactor, and the chlorine formation activity per unit mass of Catalyst d was calculated according to the following equation:

Chlorine formation activity per unit mass of the catalyst (mol/min.g-cat.) =  
15 Amount of outlet chlorine formed per unit time (mol/min.) / weight of catalyst (g)

The results are as follows:

Initial:	$6.9 \times 10^{-4}$ mol/min.g-cat.
After 502 hours:	$5.9 \times 10^{-4}$ mol/min.g-cat.
20 After 984 hours:	$5.1 \times 10^{-4}$ mol/min.g-cat.
After 1392 hours:	$5.4 \times 10^{-4}$ mol/min.g-cat.
After 1955 hours:	$4.7 \times 10^{-4}$ mol/min.g-cat.
After 2239 hours:	$4.8 \times 10^{-4}$ mol/min.g-cat.

From the above results, it can be seen that Catalyst d  
25 had the high catalytic activity, and could produce chlorine

with a smaller amount of the catalyst at a lower temperature. Furthermore, when Catalyst d was used in the above chlorine formation reaction, it had a longer life.

#### Example 12

5 1) The first catalyst of this Example was prepared as follows.

To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (60.0 g), pure water (44.8 g) and titanium oxide sol (CSB 10 (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) were added, mixed and well kneaded at room temperature while drying.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm $\phi$ , and dried under air 15 at 60°C for 4 hours to obtain white noodle-form titanium oxide (58.0 g).

The obtained titanium oxide solid was heated under air from room temperature to 700°C over 1.9 hours and calcined at the same temperature for 3 hours to obtain white noodle- 20 form titanium oxide (56.5 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide carrier.

Then, the carrier (20.0 g) was impregnated with an 25 aqueous solution of commercially available ruthenium

chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 38.2 mass %) (2.39 g) dissolved in pure water (10.4 g), dried at room temperature overnight, and further dried at 60°C for 2 hours.

5        The obtained solid was heated under air from room temperature to 350°C over 1.8 hours while supplying an air at a flow rate of 200 ml/min. and calcined at the same temperature for 2 hours to obtain an extruded black ruthenium oxide catalyst supported on titanium oxide (20.9 g).

10        The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 5.6 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

15         $[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 4.3 \text{ mass \%}$

The obtained catalyst is named "Catalyst b".

#### Measuring method of EXAFS

20        The EXAFS spectrum at the Ru K absorption edge of Catalyst b was measured with the XAFS spectrometer installed at the Beamline 10B (BL-10B) in the Photon Factory, the Institute of Materials Structure Science, the High Energy Accelerator Research Organization. Using the monochromater employed a Si (311) channel-cut crystal, the intensity of incident X-ray ( $I_0$ ) was measured with a 17 cm

25        ion chamber filled with argon as a gas at room temperature,



## Analysis of EXAFS

25 As ruthenium oxide having a particle size of 10 nm or







reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was thoroughly mixed with the commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (20 g) to dilute Catalyst b, and diluted Catalyst b was charged in the quartz reactor. The catalyst a and b were charged in a reactor in this order from the inlet of the reactor. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in the catalyst layer in the range of 320-360±1°C, and maintain the internal temperature (hot spot) at 360±1°C. Then, the reaction was continued for 50 hours under the above conditions. After that, Catalyst b was recovered, and recovered Catalyst b was subjected to the measurement of its chlorine formation activity.

That is, recovered Catalyst b (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1. When 3.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst D(b) was  $5.75 \times 10^{-4}$  mol/min.g-cat.

Then, the peak intensity ratio B(b) of Catalyst b after the reaction was calculated in the same way as in the calculation of the peak intensity ratio A(b) by the EXAFS method. The B(b) ratio was 0.80.

5 Thus, B(b)/A(b) was 1.16.

The ratio of the catalytic activity after the 50 hours reaction to the initial catalytic activity, D(b)/C(b) was 0.88.

#### Example 13

10 1) A catalyst of this Example was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (800 g) and an organic binder (16 g) were well mixed. To this mixture, pure water (360 g) and titanium oxide sol (CSB  
15 (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (133 g) were added, mixed and well kneaded.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm $\phi$ , and dried under air  
20 at 110°C for 14 hours to obtain white noodle-form titanium oxide. The noodle-form solid was cut to a length of about 5 to 3 mm to obtain white titanium oxide solid.

Then, the solid (450 g) was heated from room  
temperature to 700°C over 3 hours and calcined at the same  
25 temperature for 3 hours to obtain the extruded white

titanium oxide carrier (434 g).

Thereafter, the carrier (50.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 39.6 mass %) (5.78 g) dissolved in pure water (23.5 ml), dried at room temperature for 3 hours and dried at 60°C for 20 minutes, and then at 110°C for 14 hours.

The obtained solid was heated from room temperature to 300°C over 2.0 hours while supplying an air at a flow rate of 1 l/min. and calcined at the same temperature for 2 hours to obtain an extruded black ruthenium oxide catalyst supported on titanium oxide (52.8 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 5.65 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 4.3 \text{ mass \%}$$

The obtained catalyst is named "Catalyst b".

With Catalyst b, the peak intensity ratio A(b) of the radial distribution function was measured by the EXAFS method in the same manner as that in Example 12.

The peak intensity ratio A(b) was 0.49, when it was calculated by dividing the peak intensity of Catalyst b by the peak intensity of ruthenium oxide having the particle size of 10 nm or more with respect to the peak of the

radial distribution function near 0.32 nm.

The above-obtained ruthenium oxide catalyst supported on titanium oxide (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1. When 1.8 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $6.9 \times 10^{-4}$  mol/min.g-cat.

2) To measure B(b) of Catalyst b, the following test reaction was carried out:

Catalyst a (0.25 g) was charged in a quartz tube reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was diluted by mixing with the commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (20 g), and diluted Catalyst b was charged in the quartz reactor. The catalyst a and b were charged in a reactor in this order from the inlet of the reactor. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in the catalyst layer in the range of 320-360±1°C, and



at the same temperature for 3 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina (35.4 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- $\alpha$ -alumina carrier.

Then, the carrier (30.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 38.2 mass %) (2.39 g) dissolved in pure water (7.00 g), dried at room temperature overnight and further dried at 60°C for 2 hours.

The obtained solid was heated from room temperature to 350°C over 1.8 hours while supplying an air at a flow rate of 200 ml/l and calcined at the same temperature for 2 hours to obtain an extruded black ruthenium oxide catalyst supported on titanium oxide- $\alpha$ -alumina (31.0 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.8 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.9 \text{ mass \%}$$

The obtained catalyst was named "Catalyst b".

With Catalyst b, the peak intensity ratio A(b) of the radial distribution function was measured by the EXAFS method in the same manner as that in Example 12.

The peak intensity ratio A(b) was 0.66, when it was

calculated by dividing the peak intensity of Catalyst b by the peak intensity of ruthenium oxide having the particle size of 10 nm or more with respect to the peak of the radial distribution function near 0.32 nm.

5 The above-obtained ruthenium oxide catalyst supported on titanium oxide- $\alpha$ -alumina (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the oxygen gas was supplied at a flow  
10 rate of 206 ml/min. and the internal temperature (hot spot) was maintained at 301°C. When 2 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst C(b) was  $5.15 \times 10^{-4}$  mol/min.g-cat.

To measure the chlorine formation activity after 50  
15 hours reaction D(b), the following test reaction was carried out.

Catalyst a (0.25 g), which is the same as Catalyst a used in Example 12, was charged in a quartz tube reactor having an inner diameter of 14 mm without dilution from the  
20 inlet of the reactor. Catalyst b (2.50 g) was diluted by mixing with the commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (20 g), and diluted Catalyst b was charged in the quartz reactor. The catalyst a and b were charged in a  
25 reactor in this order from the inlet of the reactor. Then,

hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in the catalyst layer in the range of 320-360±1°C, and maintain the internal temperature (hot spot) at 360±1°C. Then, the reaction was continued for 50 hours under the above conditions. After that, Catalyst b was recovered, and recovered Catalyst b was subjected to the measurement of its chlorine formation activity.

That is, recovered Catalyst b (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that hydrogen chloride was supplied at a flow rate of 190 ml/min. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst D(b) was  $4.1 \times 10^{-4}$  mol/min.g-cat.

Thus, the ratio of the catalytic activity after the 50 hours reaction to the initial catalytic activity, D(b)/C(b) was 0.80.

#### Example 15

A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal)





while supplying an air at a flow rate of 200 ml/l and calcined at the same temperature for 2 hours to obtain an extruded black ruthenium oxide catalyst supported on titanium oxide- $\alpha$ -alumina (20.2 g).

5 The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.8 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.9 \text{ mass \%}$$

10 The obtained catalyst was named "Catalyst b".

With Catalyst b, the peak intensity ratio A(b) of the radial distribution function was measured by the EXAFS method in the same manner as that in Example 12.

The peak intensity ratio A(b) was 0.49, when it was  
15 calculated by dividing the peak intensity of Catalyst b by the peak intensity of ruthenium oxide having the particle size of 10 nm or more with respect to the peak of the radial distribution function near 0.32 nm.

The above-obtained ruthenium oxide catalyst supported  
20 on titanium oxide- $\alpha$ -alumina (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the oxygen gas was supplied at a flow rate of 193 ml/min. When 2.2 hours after the start of the  
25 reaction, the chlorine formation activity per unit mass of

the catalyst C(b) was  $5.5 \times 10^{-4}$  mol/min.g-cat.

To measure the chlorine formation activity D(b) after 50 hours reaction, the following test reaction was carried out.

5 Catalyst a (0.25 g), which is the same as Catalyst a used in Example 12, was charged in a quartz tube reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was diluted by  
10 mixing with the commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (20 g), and diluted Catalyst b was charged in the quartz reactor. The catalyst a and b were charged in a reactor in this order from the inlet of the reactor. Then, hydrogen chloride gas and oxygen gas were supplied in the  
15 quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in the catalyst  
20 layer in the range of 320-360 $\pm$ 1°C, and maintain the internal temperature (hot spot) at 360 $\pm$ 1°C. Then, the reaction was continued for 50 hours under the above conditions. After that, Catalyst b was recovered, and recovered Catalyst b was subjected to the measurement of  
25 its chlorine formation activity.



oxide- $\alpha$ -alumina. The noodle-form solid was cut to a length of about 3 to 5 mm to obtain white titanium oxide- $\alpha$ -alumina solid.

Then, a sample of 450 g from the obtained solid was  
5 heated from room temperature to 600°C over 3 hours and calcined at the same temperature for 3 hours to obtain the extruded white titanium oxide- $\alpha$ -alumina carrier (443 g).

Thereafter, the carrier (50.0 g) was impregnated with an aqueous solution of commercially available ruthenium  
10 chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 39.6 mass %) (1.96 g) dissolved in pure water (13.4 ml), kept standing at room temperature for 3 hours and dried at 60°C for 20 minutes, and then at 110°C for 14 hours.

The obtained solid (52.7 g) was heated from room  
15 temperature to 300°C over 2.0 hours while supplying an air at a flow rate of 1 l/min. and calcined at the same temperature for 2 hours to obtain an extruded black ruthenium oxide catalyst supported on titanium oxide (50.8 g).

20 The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.0 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.5 \text{ mass \%}$$

25 The obtained catalyst is named "Catalyst b".

The obtained ruthenium oxide catalyst supported on titanium oxide- $\alpha$ -alumina (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the internal temperature (hot spot) was maintained at 299°C. When 2.1 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst C(b) was  $3.83 \times 10^{-4}$  mol/min.g-cat.

To measure the chlorine formation activity D(b) after 50 hours reaction, the following test reaction was carried out.

Catalyst a (0.25 g), which is the same as Catalyst a used in Example 12, was charged in a quartz tube reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was diluted by mixing with the commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (20 g), and diluted Catalyst b was charged in the quartz reactor. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in

the catalyst layer in the range of  $320-360\pm 1^{\circ}\text{C}$ , and maintain the internal temperature (hot spot) at  $360\pm 1^{\circ}\text{C}$ . Then, the reaction was continued for 50 hours under the above conditions. After that, Catalyst b was recovered, and recovered Catalyst b was subjected to the measurement of its chlorine formation activity.

That is, recovered Catalyst b (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that hydrogen chloride was supplied at a flow rate of 190 ml/min. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst D(b) was  $3.26 \times 10^{-4}$  mol/min.g-cat.

Thus, the ratio of the catalytic activity after the 50 hours reaction to the initial catalytic activity,  $D(b)/C(b)$  was 0.85.

#### Example 17

A catalyst was prepared as follows.

To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (60.0 g), pure water (44.7 g) and titanium oxide sol (CSB ( $\text{TiO}_2$  content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) were added, mixed and well kneaded at room temperature.

The mixture was molded by extrusion in the form of

noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide (57.3 g).

The obtained titanium oxide solid was heated under air from room temperature to 700°C over 1.9 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide (55.6 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide carrier.

Then, the carrier (30.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 38.2 mass %) (3.58 g) dissolved in pure water (10.1 g) and dried at room temperature overnight to obtain the supported ruthenium chloride solid (41.2 g).

Then, 10.3 g of this solid from the supported ruthenium chloride one was dried at 350°C for 2 hours while supplying nitrogen gas at a flow rate of 192 ml/min. to obtain an extruded black catalyst supported on titanium oxide (7.88 g).

The above-obtained catalyst supported on titanium oxide (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1. When 1.8 hours after



the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $6.15 \times 10^{-4}$  mol/min.g-cat.

#### Example 18

1) A catalyst was prepared as follows.

5 To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (50.0 g), pure water (35.1 g) and titanium oxide sol (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (6.6 g) were added and kneaded.

10 The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 2 hours to obtain white noodle-form titanium oxide (40.2 g). The same operation was repeated. In total, 80.7 g of the white noodle-form titanium oxide was obtained.

15 The obtained titanium oxide solid was heated under air from room temperature to 700°C over 1.9 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide.

20 After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide carrier.

25 Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride (RuCl<sub>3</sub>.nH<sub>2</sub>O, ruthenium content: 37.3 mass %) (2.55 g) dissolved in pure water (8.65 g), and dried at 60°C for



of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded black ruthenium oxide catalyst supported  
5 on titanium oxide.

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 5.9 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

10  $[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 4.5 \text{ mass } \%$

With Catalyst b, the peak intensity ratio A(b) of the radial distribution function was measured by the EXAFS method in the same manner as that in Example 12.

The peak intensity ratio A(b) was 0.41, when it was  
15 calculated by dividing the peak intensity of Catalyst b by the peak intensity of ruthenium oxide having the particle size of 10 nm or more with respect to the peak of the radial distribution function near 0.32 nm.

The above-obtained ruthenium oxide catalyst supported  
20 on titanium oxide (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the internal temperature (hot spot) was maintained at 299°C. When 2.7 hours after the start of the reaction, the  
25 chlorine formation activity per unit mass of the catalyst

was  $8.75 \times 10^{-4}$  mol/min.g-cat.

2) To measure B(b) of Catalyst b, the following test reaction was carried out:

Catalyst a (0.25 g), which is the same as Catalyst a used in Example 12, was charged in a quartz tube reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was diluted by mixing with the commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (20 g), and diluted Catalyst b was charged in the quartz reactor. The catalysts a and b were charged in a reactor in this order from the inlet of the reactor. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in the catalyst layer in the range of  $320-360 \pm 1^\circ\text{C}$ , and maintain the internal temperature (hot spot) at  $360 \pm 1^\circ\text{C}$ . Then, the reaction was continued for 50 hours under the above conditions. After that, Catalyst b was recovered, and recovered Catalyst b was subjected to the measurement of its chlorine formation activity.

That is, recovered Catalyst b (2.5 g) was filled in

the reactor in the same manner as that in Example 1 except that Catalyst b was diluted with the commercially available spherical  $\alpha$ -alumina having a diameter of 2 mm (20 g) by mixing them thoroughly and then charged in the reactor, and the reaction was carried out in the same manner as that in Example 1. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $6.5 \times 10^{-4}$  mol/min.g-cat.

Then, the peak intensity ratio B(b) of Catalyst b after the reaction was calculated in the same manner as in the calculation of the peak intensity ratio A(b) by the EXAFS method. The B(b) ratio was 0.62

Thus, B(b)/A(b) was 1.51.

The ratio of the catalytic activity after the 50 hours reaction to the initial catalytic activity, D(b)/C(b) was 0.74.

#### Example 19

A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (25.0 g) and aluminum oxide powder (AL-31 manufactured by Sumitomo Chemical Co., Ltd.) (25.0 g) were thoroughly mixed. To the mixture, pure water (18.9 g) and titanium oxide sol (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (6.6 g) were added and kneaded.

This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 2 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina (47.1 g).

5        24.5 Grams of the solid from the white noodle-form titanium oxide- $\alpha$ -alumina was heated under air from room temperature to 600°C over 1.7 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina.

10        After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- $\alpha$ -alumina carrier.

Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride (RuCl<sub>3</sub>.nH<sub>2</sub>O, ruthenium content: 37.3 mass %) (0.805 g) dissolved in pure water (5.82 g) and dried at 60°C for 2 hours.

Then, the obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (4.2 g), pure water (120 g) and hydrazine monohydrate (1.03 g). Bubbling was observed as soon as the dried solid was dipped in the solution. After 60 minutes, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and



$$[\text{Ru}/(\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.5 \text{ mass } \%$$

The above-obtained ruthenium oxide catalyst supported on titanium oxide- $\alpha$ -alumina (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1.

To measure the chlorine formation activity D(b) after 50 hours reaction, the following test reaction was carried out.

Catalyst a (0.25 g), which is the same as Catalyst a used in Example 12, was charged in a quartz tube reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was diluted by mixing with the commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (20 g), and diluted Catalyst b was charged in the quartz reactor. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in the catalyst layer in the range of 320-360±1°C, and maintain the internal temperature (hot spot) at 360±1°C. Then, the reaction was continued for 50 hours under the



above conditions. After that, Catalyst b was recovered, and recovered Catalyst b was subjected to the measurement of its chlorine formation activity.

That is, recovered Catalyst b (2.5 g) was filled in  
5 the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1.

#### Example 20

A catalyst was prepared as follows.

10 To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (60.0 g), pure water (44.7 g) and titanium oxide sol (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) were added, mixed and well  
15 kneaded at room temperature.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide (57.3 g).

20 The obtained titanium oxide solid was heated under air from room temperature to 700°C over 1.9 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide (55.6 g).

After calcination, the noodle-form solid was cut to a  
25 length of about 5 mm to obtain an extruded white titanium

oxide carrier.

Then, the carrier (30.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 38.2 mass %) (3.58 g) dissolved in pure water (10.1 g) and dried at room temperature overnight to obtain the supported ruthenium chloride solid (41.2 g).

Then, 10.3 g of this solid from the supported ruthenium chloride one was dried at  $150^\circ\text{C}$  for 2 hours while supplying nitrogen gas at a flow rate of 192 ml/min. to obtain an extruded black ruthenium chloride catalyst supported on titanium oxide (8.14 g).

The calculated content of ruthenium chloride was as follows:

$$[\text{RuCl}_2 / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 8.56 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 4.17 \text{ mass \%}$$

The above-obtained ruthenium chloride catalyst supported on titanium oxide (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the internal temperature (hot spot) was maintained at  $301^\circ\text{C}$ . When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $6.05 \times 10^{-4} \text{ mol/min.g-cat.}$

Example 21

10.3 Grams of solid from the undried supported ruthenium chloride on the titanium oxide carrier, which is the solid prepared in Example 20, was dried at 60°C for 2 hours while supplying nitrogen gas at a flow rate of 200 ml/min. to obtain an extruded black ruthenium chloride catalyst supported on titanium oxide (8.40 g).

The calculated content of ruthenium chloride was as follows:

$$10 \quad [\text{RuCl}_2 / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 8.56 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 4.17 \text{ mass \%}$$

The above-obtained ruthenium chloride catalyst supported on titanium oxide (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $5.85 \times 10^{-4}$  mol/min.g-cat.

20 Example 22

A catalyst was prepared as follows.

To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (60.0 g), pure water (44.7 g) and titanium oxide sol (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical

$$25 \quad [\text{Ru}/(\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 4.17 \text{ mass } \%$$

The above-obtained ruthenium chloride catalyst supported on titanium oxide (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in  
 5 Example 1. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $7.0 \times 10^{-4}$  mol/min.g-cat.

#### Example 23

A catalyst was prepared as follows.

10 To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (60.0 g), pure water (44.8 g) and titanium oxide sol (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) were added and well kneaded at  
 15 room temperature.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide (58.0 g).

20 The obtained titanium oxide solid was heated under air from room temperature to 700°C over 1.9 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide (56.5 g).

After calcination, the noodle-form solid was cut to a  
 25 length of about 5 mm to obtain an extruded white titanium

oxide carrier.

Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 38.2 mass %) (2.39 g) dissolved in pure water (10.4 g), dried at room temperature overnight and further dried under air at  $100^\circ\text{C}$  for 2 hours to obtain an extruded black ruthenium chloride catalyst supported on titanium oxide (14.3 g).

The calculated content of ruthenium chloride was as follows:

$$[\text{RuCl}_2 / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 8.56 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 4.17 \text{ mass \%}$$

The above-obtained ruthenium chloride catalyst supported on titanium oxide was filled in the reactor in the same manner as that in Example 1 except that the ruthenium chloride catalyst supported on titanium oxide (1 g) was diluted with the commercially available spherical  $\alpha$ -alumina carrier having a particle size of 2 mm (20 g) by mixing, and the reaction was carried out in the same manner as that in Example 1. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $11.8 \times 10^{-4} \text{ mol/min.g-cat.}$

#### Example 24

1) The solid from the undried supported ruthenium

chloride on the titanium oxide carrier, which is prepared in Example 23, was dried under air at 60°C for 2 hours to obtain an extruded black ruthenium chloride catalyst supported on titanium oxide (8.0 g).

5           The calculated content of ruthenium chloride was as follows:

$$[\text{RuCl}_2/(\text{RuCl}_2+\text{TiO}_2)] \times 100 = 8.56 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuCl}_2+\text{TiO}_2)] \times 100 = 4.17 \text{ mass \%}$$

10           This catalyst was named "Catalyst b".

The above-obtained ruthenium chloride catalyst supported on titanium oxide (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in  
15 Example 1. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst E(b) was  $6.45 \times 10^{-4}$  mol/min.g-cat.

The same ruthenium chloride catalyst supported on titanium oxide (1.0 g) was filled in the reactor in the  
20 same manner as that in Example 1 except that the ruthenium chloride catalyst supported on titanium oxide (1 g) was diluted with the commercially available spherical  $\alpha$ -alumina carrier having a particle size of 2 mm (20 g) by mixing, and the reaction was carried out in the same manner as that  
25 in Example 1. When 2.0 hours after the start of the

reaction, the chlorine formation activity per unit mass of the catalyst was  $11.2 \times 10^{-4}$  mol/min.g-cat.

2) The second catalyst of this Example was prepared as follows.

5 A commercially available  $\alpha$ -alumina (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (30.1 g), ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 37.3 mass %) (1.62 g), pure water (3.0 g) and alumina sol (ALUMINA SOL 200 manufactured by Nissan Chemical Industries, 10 Ltd.) (8.53 g) were thoroughly mixed. A dry air was blown onto the mixture at room temperature to dry the mixture until an adequate viscosity was reached.

This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm $\phi$ , and dried under air 15 at 60°C for 4 hours to obtain brown noodle-form ruthenium oxide- $\alpha$ -alumina.

The obtained noodle-form solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain gray noodle-form 20 ruthenium oxide catalyst supported on  $\alpha$ -alumina (25.8 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.5 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

25 
$$[\text{Ru} / (\text{RuO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.9 \text{ mass \%}$$



The obtained catalyst was named "Catalyst a".

3) To measure the chlorine formation activity after 50 hours reaction F(b), the following test reaction was carried out.

Catalyst a (0.25 g) was charged in a quartz tube reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was diluted by mixing with the commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (20 g), and diluted Catalyst b was charged in the quartz reactor. The catalysts a and b were charged in a reactor in this order from the inlet of the reactor. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in the catalyst layer in the range of 320-360±1°C, and maintain the hot spot of Catalyst b at 360±1°C. Then, the reaction was continued for 50 hours under the above conditions. After that, Catalyst b was recovered, and recovered Catalyst b was subjected to the measurement of its chlorine formation activity.

That is, recovered Catalyst b (2.4 g) was filled in

the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1. When 1.8 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst F(b) was  $7.05 \times 10^{-4}$  mol/min.g-cat.

Thus, the ratio of the catalytic activity after the 50 hours reaction to the initial catalytic activity, F(b)/E(b) was 1.09.

#### Example 25

A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (48.0 g) and aluminum oxide powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (12.0 g) were thoroughly mixed. To the mixture, pure water (39.5 g) and titanium oxide sol (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) were added and well kneaded at room temperature.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina (57.0 g).

The obtained titanium oxide- $\alpha$ -alumina solid was heated under air from room temperature to 600°C over 1.7 hours and calcined at the same temperature for 3 hours to obtain

white noodle-form titanium oxide- $\alpha$ -alumina (55.6 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- $\alpha$ -alumina carrier.

5 Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 38.2 mass %) (1.99 g) dissolved in pure water (10.1 g), dried at room temperature overnight and further dried under air at 60°C  
10 for 2 hours to obtain an extruded black ruthenium chloride catalyst supported on titanium oxide (21.9 g).

The calculated content of ruthenium chloride was as follows:

$$[\text{RuCl}_2 / (\text{RuCl}_2 + \text{TiO}_2 + \alpha\text{-alumina})] \times 100 = 7.24 \text{ mass \%}$$

15 The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuCl}_2 + \text{TiO}_2 + \alpha\text{-alumina})] \times 100 = 3.52 \text{ mass \%}$$

The above-obtained ruthenium chloride catalyst supported on the titanium oxide- $\alpha$ -alumina carrier (2.5 g) was filled in the reactor in the same manner as that in  
20 Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the internal temperature (hot spot) was 301°C. When 2.5 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $6.95 \times 10^{-4}$  mol/min.g-cat.

25 Example 26

1) A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (30.0 g) and aluminum oxide powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (30.0 g) were thoroughly mixed. To the mixture, pure water (22.5 g) and titanium oxide sol (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) were added, mixed and well kneaded at room temperature.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina (56.3 g).

The obtained titanium oxide- $\alpha$ -alumina solid was heated under air from room temperature to 600°C over 1.7 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina (55.4 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- $\alpha$ -alumina carrier.

Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride (RuCl<sub>3</sub>.nH<sub>2</sub>O, ruthenium content: 38.2 mass %) (1.59 g) dissolved in pure water (6.40 g), dried at room temperature overnight and further dried under air at 60°C

for 2 hours to obtain an extruded black ruthenium chloride catalyst supported on titanium oxide (21.5 g).

The calculated content of ruthenium chloride was as follows:

5           
$$[\text{RuCl}_2 / (\text{RuCl}_2 + \text{TiO}_2 + \alpha\text{-alumina})] \times 100 = 5.87 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuCl}_2 + \text{TiO}_2 + \alpha\text{-alumina})] \times 100 = 2.86 \text{ mass } \%$$

The above-obtained ruthenium chloride catalyst supported on titanium oxide- $\alpha$ -alumina (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the internal temperature (hot spot) was maintained at 301°C. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst E(b) was  $4.98 \times 10^{-4}$  mol/min.g-cat.

2) To measure the chlorine formation activity after 50 hours reaction F(b), the following test reaction was carried out.

Catalyst a (0.25 g), which was a ruthenium chloride catalyst supported on  $\alpha$ -alumina prepared in the same manner as that in Example 24, was charged in a quartz tube reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was diluted by mixing with the commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by

NIKKATO) (20 g), and diluted Catalyst b was charged in the quartz reactor. The catalysts a and b were charged in a reactor in this order from the inlet of the reactor. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in the catalyst layer in the range of 320-360±1°C, and maintain the hot spot of Catalyst b at 360±1°C. Then, the reaction was continued for 50 hours under the above conditions. After that, Catalyst b was recovered, and recovered Catalyst b was subjected to the measurement of its chlorine formation activity.

That is, recovered Catalyst b (2.3 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst F(b) was  $4.96 \times 10^{-4}$  mol/min.g-cat.

Thus, the ratio of the catalytic activity after the 50 hours reaction to the initial catalytic activity, F(b)/E(b) was 1.0.

A catalyst was prepared as follows.

Commercially available ruthenium chloride hydrate ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 35.5 mass %) (0.70 g) was dissolved in pure water (4.0 g). After the aqueous  
5 solution was sufficiently stirred, it was dropwise added to silica (CARIACT G-10 manufactured by Fuji Silysia Chemical Co.) (5.0 g), the particle sizes of which had been adjusted in the range between 0.85 and 1.4 mm and which had been dried under air at 500°C for 1 hour to support ruthenium  
10 chloride on the silica particles. The supported one was heated from room temperature to 100°C over 30 minutes while supplying nitrogen gas at a flow rate of 100 ml/min. and dried at the same temperature for 2 hours, followed by spontaneous cooling to room temperature to obtain a black  
15 solid.

The obtained solid was heated from room temperature to 250°C over 1.5 hours while supplying the air at a rate of 100 ml/min. and dried at the same temperature for 3 hours, followed by spontaneous cooling to room temperature to  
20 obtain a black ruthenium chloride catalyst supported on silica.

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuCl}_3 \cdot 3\text{H}_2\text{O} + \text{SiO}_2)] \times 100 = 4.5 \text{ mass \%}$$

The above-obtained ruthenium chloride catalyst  
25 supported on silica (2.5 g) without dilution was filled in

the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that hydrogen chloride and oxygen were supplied at flow rates of 202 ml/min. and 213 ml/min., respectively. When 1.7 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $0.49 \times 10^{-4}$  mol/min.g-cat.

#### Comparative Example 2

A catalyst was prepared as follows.

Spherical titanium oxide (CS-300 manufactured by Sakai Chemical Industry Co., Ltd.) was ground with a mortar to obtain titanium oxide powder. The titanium oxide powder (8.0 g) and ruthenium dioxide powder (0.53 g) were mixed in a mortar while grinding, followed by molding in the form of particles having sizes of 0.85 to 1.4 mm to obtain a ruthenium oxide-titanium oxide mixed catalyst. The calculated content of ruthenium oxide was 6.2 mass %, and that of ruthenium was 4.7 mass %.

The above-obtained ruthenium oxide-titanium oxide mixed catalyst (2.5 g) was diluted by mixing with a titanium oxide carrier having adjusted particle sizes of 0.85 to 1.4 mm (5 g), and the diluted catalyst was charged in a quartz tube reactor having an inner diameter of 12 mm. Then, the reaction was carried out in the same manner as that in Example 1 except that hydrogen chloride and oxygen



were supplied at flow rates of 199 ml/min. and 194 ml/min., respectively, and the internal temperature (hot spot) was maintained at 299°C. When 2.3 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $0.83 \times 10^{-4}$  mol/min.g-cat.

### Comparative Example 3

A catalyst was prepared as follows.

Commercially available tetraethyl orthosilicate (41.7 g) was dissolved in ethanol (186 ml). To the solution, titanium tetraisopropoxide (56.8 g) was added, and the mixture was stirred at room temperature for 30 minutes. Then, to this solution, an aqueous solution was dropwise added, which was prepared by well mixing ethanol (93 ml) with a 0.01 mol/l aqueous solution of acetic acid that had been prepared by dissolving acetic acid (0.14 g) in pure water (233 ml). White precipitates formed as the aqueous solution was dropwise added. After the dropwise addition, the mixture was stirred at room temperature for 30 minutes. Thereafter, the mixture was heated to reflux on an oil bath maintained at 102°C for 1 hour while stirring, during which the temperature of the liquid was 80°C. Then, the liquid was spontaneously cooled, filtrated with a glass filter, washed with water (500 ml) and again filtrated. This operation was repeated twice. Thereafter, the product was dried under air at 60°C for 4 hours, heated from room

temperature to 550°C over 1 hour, and calcined at the same temperature for 3 hours to obtain a white solid (27.4 g). The white solid was ground to obtain titania-silica powder.

The obtained titania-silica powder (8.0 g) was  
 5 impregnated with an aqueous solution of commercially available ruthenium chloride hydrate ( $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , ruthenium content: 35.5 mass %) (1.13 g) in pure water (8.2 g), and dried at 60°C for 1 hour to support ruthenium chloride on the titania-silica powder. Then, the titania-silica powder  
 10 supporting ruthenium chloride was reduced by heating it from room temperature to 300°C over 1.5 hours and then at the same temperature for 1 hour while supplying the mixture of hydrogen gas and nitrogen gas at flow rates of 50 ml/min. and 100 ml/min., respectively, followed by spontaneously  
 15 cooling to room temperature to obtain a grayish brown metal ruthenium supported on the titania-silica powder (8.4 g).

The obtained metal ruthenium supported on the titania-silica powder (8.4 g) was heated from room temperature to 600°C over 3 hours and 20 minutes and calcined at the same  
 20 temperature for 3 hours while supplying an air at a flow rate of 100 ml/min. to obtain the gray powder (8.5 g). The gray powder was molded in the form of particles having sizes of 0.85 to 1.4 mm to obtain a ruthenium oxide catalyst supported on titania-silica.

25 The calculated content of ruthenium oxide was as

follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \text{SiO}_2)] \times 100 = 6.2 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \text{SiO}_2)] \times 100 = 4.7 \text{ mass } \%$$

5        The obtained ruthenium oxide catalyst supported on  
titania-silica (2.5 g) without dilution was charged in the  
quartz reactor tube, and the reaction was carried out in  
the same manner as that in Example 1 except that hydrogen  
chloride gas and oxygen gas were supplied at flow rates of  
10    180 ml/min. and 180 ml/min., respectively.

When 1.8 hours after the start of the reaction, the  
chlorine formation activity per unit mass of the catalyst  
was  $0.46 \times 10^{-4}$  mol/min.g-cat.

#### Comparative Example 4

15        A catalyst was prepared as follows.

A spherical titanium oxide carrier having a diameter  
of 1 to 2 mm (CS-300S-12 manufactured by Sakai Chemical  
Industry Co., Ltd.) (10.1 g) was impregnated with an  
aqueous solution of commercially available ruthenium  
20    chloride hydrate ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 37.3  
mass %) (1.34 g) in pure water (3.7 g), and dried under air  
at 60°C for 4 hours to obtain a dark brown solid. This  
dark brown solid was reduced by heating it from room  
temperature to 250°C over 2 hours and then at the same  
25    temperature for 8 hours while supplying the mixture of

hydrogen gas and nitrogen gas at flow rates of 20 ml/min. and 200 ml/min., respectively to obtain the black solid (10.3 g).

Then, the obtained solid was heated under air from  
5 room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain a black ruthenium oxide catalyst supported on titanium oxide (10.6 g).

The calculated content of ruthenium oxide was as follows:

10 
$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 6.1 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 4.7 \text{ mass } \%$$

The obtained ruthenium oxide catalyst supported on titanium oxide (2.5 g) was diluted with the commercially  
15 available spherical titanium oxide having a diameter of 1 to 2 mm (CS-300S-12 manufactured by Sakai Chemical Industry Co., Ltd.) (5 g) by mixing them thoroughly and then charged in the reactor in the same manner as in Example 1, and the reaction was carried out in the same manner as that in  
20 Example 1 except that hydrogen chloride gas and oxygen gas were supplied at flow rates of 187 ml/min. and 199 ml/min., respectively.

When 2 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst  
25 was  $2.89 \times 10^{-4}$  mol/min.g-cat.

## Comparative Example 5

A catalyst was prepared as follows.

A spherical metal ruthenium catalyst supported on titanium oxide having a diameter of 1 to 2 mm (5 mass % supported on anatase titanium oxide) (manufactured by N.E. Chemcat) was impregnated with a 0.5 mol/l aqueous solution of potassium chloride to an extent that the solution oozed out on the surface of the catalyst, and dried under air at 60°C for 1 hour. The same operation was repeated twice.

10 The impregnated amount of the aqueous solution of potassium chloride was 3.31 g in the first operation and 3.24 g in the second operation. Thus, the total impregnated amount of the aqueous solution of potassium chloride was 6.55 g. The calculated molar ratio of potassium chloride to

15 ruthenium was 0.66.

The dried catalyst was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours. Then, the calcined catalyst was washed with pure water (500 ml) for 30 minutes, followed by

20 filtration. The washing and filtration were repeated five time. An aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained. After washing, the solid was dried at 60°C for 4 hours to obtain black spherical ruthenium oxide

25 supported on titanium oxide (9.9 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 6.6 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

5  $[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 5.0 \text{ mass \%}$

The obtained ruthenium oxide catalyst supported on titanium oxide (2.5 g) was diluted with the commercially available spherical titanium oxide having a diameter of 1 to 2 mm (CS-300S-12 manufactured by Sakai Chemical Industry Co., Ltd.) (5 g) by mixing them thoroughly and then charged in the reactor in the same manner as in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that hydrogen chloride gas and oxygen gas were supplied at flow rates of 187 ml/min. and 199 ml/min., respectively.

15

When 2 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $4.03 \times 10^{-4}$  mol/min.g-cat.

#### Comparative Example 6

20 1) The first catalyst of this Comparative Example was prepared as follows.

To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (50.0 g), pure water (33.6 g) and titanium oxide sol (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical

25

Industry Co., Ltd.) (6.59 g) were added and kneaded. A dry  
air was blown onto the kneaded mixture at room temperature  
to dry the mixture until an adequate viscosity was reached.  
The mixture was molded by extrusion in the form of noodles  
5 having a diameter of 1.5 mm $\phi$ , and dried under air at 60°C  
for 4 hours.

Separately, to titanium oxide powder (STR-60R (100 %  
rutile crystal) manufactured by Sakai Chemical Industry Co.,  
Ltd.) (20.0 g), pure water (13.3 g) and titanium oxide sol  
10 (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai  
Chemical Industry Co., Ltd.) (2.65 g) were added and  
kneaded. A dry air was blown onto the kneaded mixture at  
room temperature to dry the mixture until an adequate  
viscosity was reached. The mixture was molded by extrusion  
15 in the form of noodles having a diameter of 1.5 mm $\phi$ , and  
dried under air at 60°C for 4 hours.

The two portions of the dried noodle-form solids were  
mixed and heated under air from room temperature to 500°C  
over 1.4 hours and calcined at the same temperature for 3  
20 hours to obtain white noodle-form titanium oxide (64.8 g).

After calcination, the noodle-form solid was cut to a  
length of about 5 mm to obtain an extruded white titanium  
oxide carrier.

Then, the carrier (62.0 g) was impregnated with an  
25 aqueous solution of commercially available ruthenium

chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 37.3 mass %) (5.04 g) dissolved in pure water (34.1 g), and dried at 60°C for 2 hours.

The obtained solid was dipped in a solution containing  
 5 2N aqueous solution of potassium hydroxide (26.1 g), pure water (372 g) and hydrazine monohydrate (6.33 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the  
 10 recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 9.0, and that of the fifth wash liquid was 7.2.

To the filtrated solid, a 0.5 mol/l aqueous solution  
 15 of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the gray solid.

20 Then, the gray solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the bluish gray solid.

After calcination, pure water (500 ml) was added to  
 the bluish gray solid and the mixture was stirred, followed  
 25 by recovering of the solid by filtration. The same



operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to  
5 obtain an extruded bluish gray ruthenium oxide catalyst supported on titanium oxide (62.6 g).

A packing density of the obtained catalyst was 0.77.

The calculated content of ruthenium oxide was as follows:

10 
$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 3.8 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 2.9 \text{ mass } \%$$

The obtained catalyst is named "Catalyst c".

2) The second catalyst of this Comparative Example was  
15 prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (30.0 g) and aluminum oxide powder (AL-31-03 manufactured by Sumitomo Chemical Co., Ltd.) (30.0 g) were thoroughly mixed.  
20 To the mixture, pure water (19.6 g) and titanium oxide sol (CSB (TiO<sub>2</sub> content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.91 g) were added and kneaded.

-----  
This mixture was molded by extrusion in the form of  
25 noodles having a diameter of 1.5 mmφ, and dried under air

at 60°C for 4 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina.

The white noodle-form titanium oxide- $\alpha$ -alumina was heated under air from room temperature to 500°C over 1.4  
5 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- $\alpha$ -alumina (55.7 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- $\alpha$ -alumina carrier.

10 Then, the carrier (45.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 37.3 mass %) (1.83 g) dissolved in pure water (14.0 g) and dried at 60°C for 2 hours.

15 Then, the obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (9.49 g), pure water (270 g) and hydrazine monohydrate (2.30 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 60 minutes, the supernatant  
20 was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 9.2, and that of the fifth wash liquid was

25 7.2.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

5 The obtained solid was dried at 60°C for 4 hours to obtain the gray solid.

Then, the gray solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the bluish gray solid.

10 After calcination, pure water (500 ml) was added to the bluish gray solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash  
15 liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded bluish gray ruthenium oxide catalyst supported on titanium oxide- $\alpha$ -alumina (45.4 g).

The packing density of this catalyst was 0.97.

20 The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.0 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

---


$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.5 \text{ mass } \%$$

25 This catalyst was named "Catalyst b".



flowed under atmospheric pressure from the upper zone to the lower zone at flow rates of 130 ml/min. and 66 ml/min. respectively (each converted to a volume at 0°C under 101 kPa.) During the reaction, the conversion of hydrogen chloride was maintained at higher than 70 %. After 80 hours, the internal temperature (hot spot) of the upper zone in the test reactor tube was 341°C, while that of the lower zone was 302°C. At this time, the gas from the outlet of the test reactor tube was sampled by passing it through an aqueous 30 mass % potassium iodide solution, and the amount of chlorine formed and the amount of unreacted hydrogen chloride were determined by iodometric titration and neutralization titration, respectively. The conversion of hydrogen chloride was 91.0 %.

4) Thereafter, the activity of Catalyst c was measured as follows:

The activity of Catalyst c was represented by  $M(c)$ .

Catalyst c was isolated from the mixture of Catalyst c and the  $\alpha$ -alumina carrier used in the step 3). Using this Catalyst c, the activity  $M(c)$  was measured in the same manner as that for the measurement of  $M(c)$  in Example 1 except that 2.5 g of Catalyst c was diluted by mixing with the commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO)

(10 g), diluted Catalyst c was charged in a quartz reactor

tube having an inner diameter of 12 mm, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. and 192 ml/min., respectively (each converted to a volume at  
5 0°C under 101 kPa.), and the internal temperature (hot spot) was maintained at 300°C. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $7.1 \times 10^{-4}$  mol/min.g-cat.

5) In a glass test reactor tube having an inner  
10 diameter of 14 mm, in which a thermocouple-protective tube having an outer diameter of 5 mm was inserted, Catalyst a, which is the same as Catalyst a of Example 1, and above-prepared Catalysts b and c were charged in a volume ratio of 2:13:5 (a:b:c) from the inlet of a reactor. Each  
15 Catalyst had been diluted with the same volume ratio of  $\alpha$ -alumina spheres having a diameter of 2 mm (SSA 995 manufactured by NIKKATO). The charged volumes of Catalysts a, b and c were as follows:

Catalyst a: 1.73 ml (2.27 g)

20 Catalyst b: 11.25 ml (10.88 g)

Catalyst c: 4.32 ml (3.33 g)

The total volume of charged catalysts was 17.3 ml.

The upper zone of the catalyst layer was formed by Catalyst a and Catalyst b, while the lower zone of the  
25 catalyst layer was formed by Catalyst c, and each zone was

heated with a respective electric furnace.

Hydrogen chloride gas and oxygen gas were supplied and flowed under atmospheric pressure from the upper zone to the lower zone at flow rates of 130 ml/min. and 64 ml/min., respectively (each converted to a volume at 0°C under 101 kPa.) This reaction operation was carried out for 502 hours under the same conditions while maintaining the conversion of hydrogen chloride at higher than 70 %. After 502 hours, the internal temperature (hot spot) of the upper zone in the test reactor tube was 352°C, while that of the lower zone was 302°C. At this time, the gas from the outlet of the test reactor tube was sampled by passing it through an aqueous 30 mass % potassium iodide solution, and the amount of chlorine formed and the amount of unreacted hydrogen chloride were determined by iodometric titration and neutralization titration, respectively. The conversion of hydrogen chloride was 83.3 %.

6) After the step 5), Catalyst c was isolated from the mixture of Catalyst c and the  $\alpha$ -alumina carrier used in the step 5), and the activity of Catalyst c N(c) was measured in the same manner as that for the measurement of N(c) in Example 1 except that Catalyst c was diluted with a commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (10g) by mixing them thoroughly, and diluted Catalyst c was

filled in a quartz reactor tube having an inner diameter of 12 mm.

The chlorine formation activity  $N(c)$  was  $5.6 \times 10^{-4}$  mol/min.g-cat.

5 Thus,  $N(c)/M(c)$  was 0.79.

Comparative example 7

A catalyst of this Comparative Example was prepared as follows.

A spherical titanium oxide carrier (CS-300S (anatase  
10 crystal) manufactured by Sakai Chemical Industry Co., Ltd.) was ground to adjust its particle size in the range between 0.85 and 1.4 mm, and then calcined under air at 500°C for 1 hour. Then, the ground titanium oxide carrier (5.0 g) was impregnated with an aqueous solution of commercially  
15 available ruthenium chloride hydrate ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ) (1.41 g) in pure water (3.2 g), and dried by heating it from room temperature to 100°C over 30 minutes and at the same temperature for 2 hours while supplying nitrogen gas at a flow rate of 100 ml/min. Furthermore, the impregnated  
20 carrier was heated from 100°C to 250°C over 50 minutes and then at the same temperature for 3 hours to obtain a black ruthenium chloride catalyst supported on titanium oxide (10.5 g).

-----  
The calculated content of ruthenium chloride was as  
25 follows:



$$[\text{RuCl}_2 / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 9.3 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 4.5 \text{ mass } \%$$

The obtained ruthenium chloride catalyst supported on  
5 titanium oxide (2.5 g) without dilution was charged in the  
reactor in the same manner as in Example 1, and the  
reaction was carried out in the same manner as that in  
Example 1 except that hydrogen chloride gas and oxygen gas  
were supplied at flow rates of 190 ml/min. and 200 ml/min.,  
10 respectively.

When 1.7 hours after the start of the reaction, the  
chlorine formation activity per unit mass of the catalyst  
was  $2.97 \times 10^{-4}$  mol/min.g-cat.

#### Comparative Example 8

15 A catalyst of this Comparative Example was prepared as  
follows.

A spherical titanium oxide carrier (CS-300S (anatase  
crystal) manufactured by Sakai Chemical Industry Co., Ltd.)  
was ground to adjust its particle size in the range between  
20 0.85 and 1.4 mm, and then calcined under air at 500°C for 1  
hour. Then, the ground titanium oxide carrier (5.0 g) was  
impregnated with an aqueous solution of commercially  
available ruthenium chloride hydrate ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ) (0.70 g)  
in pure water (1.4 g), and dried by heating it from room  
25 temperature to 100°C over 30 minutes and at the same

temperature for 2 hours while supplying nitrogen gas at a flow rate of 100 ml/min. Furthermore, the impregnated carrier was once cooled to room temperature and heated from room temperature to 350°C over 2 hours and then at the same temperature for 3 hours while supplying an air at a flow rate of 100 ml/min. to obtain a black ruthenium oxide catalyst supported on titanium oxide (5.2 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 6.2 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 4.7 \text{ mass \%}$$

The obtained ruthenium oxide catalyst supported on titanium oxide (2.5 g) without dilution was charged in the reactor in the same manner as in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that hydrogen chloride gas and oxygen gas were supplied at flow rates of 200 ml/min. and 200 ml/min., respectively.

When 1.8 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $2.37 \times 10^{-4}$  mol/min.g-cat.

#### Comparative Example 9

A catalyst of this Comparative Example was prepared as follows.

A spherical titanium oxide carrier having a diameter of 1 to 2 mm (CS-300S-12 (anatase crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (20.0 g) was impregnated with an aqueous solution of commercially available  
 5 ruthenium chloride hydrate ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 38.2 mass %) (2.38 g) in pure water (7.0 g), and dried at room temperature overnight to obtain the carrier supporting ruthenium chloride (24.7 g). The carrier supporting  
 ruthenium chloride was dried at 60°C for 2 hours.

10 Furthermore, it was dried by heating it under a nitrogen flow (192 ml/min.) from room temperature to 150°C and then at the same temperature for 2 hours to obtain a black ruthenium chloride catalyst supported on titanium oxide (21.3 g).

15 The calculated content of ruthenium chloride was as follows:

$$[\text{RuCl}_2 / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 8.5 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 4.2 \text{ mass \%}$$

20 The obtained ruthenium chloride catalyst supported on titanium oxide (2.5 g) was charged in the reactor in the same manner as in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the  
 internal temperature (hot spot) was maintained at 301°C.

25 When 1.8 hours after the start of the reaction, the

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chlorine formation activity per unit mass of the catalyst  
was  $2.75 \times 10^{-4}$  mol/min.g-cat.

## CLAIMS

1. A supported ruthenium oxide catalyst selected from the group consisting of:

(1) a supported ruthenium oxide catalyst comprising  
5 titanium oxide which contains the rutile crystal form, and which is obtained by calcination at a temperature of at least 550°C, as a carrier;

(2) a supported ruthenium oxide catalyst having a  
carbon monoxide adsorption amount of at least 87.5 ml per  
10 one gram of ruthenium contained in the catalyst, which is measured by the following steps of:

reducing 0.1 g of said catalyst at 220°C for 60  
minutes with flowing a hydrogen gas at a flow rate of 50  
ml/min. under atmospheric pressure, and

15 conducting a metal surface area measuring method according to a carbon monoxide pulse;

(3) a supported ruthenium oxide catalyst obtained by a preparation process comprising the steps of:

supporting a ruthenium compound on a carrier,  
20 calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of  
25 hydrazine and an alkaline compound,

and

oxidizing said hydrazine-treated one.

2. The catalyst according to claim 1, which is said catalyst (2) prepared by the method for the preparation of the catalyst (3) in claim 1.

3. The catalyst according to claim 1, which is said catalyst (2) or (3), wherein said carrier is titanium oxide containing the rutile crystal form.

4. A process for producing a supported ruthenium oxide catalyst or a supported ruthenium chloride catalyst selected from the group consisting of the following processes (1) to (6):

(1) a process comprising the steps of:

supporting a ruthenium compound on a carrier consisting of titanium oxide which contains the rutile crystal form, and which is obtained by calcination at a temperature of at least 550°C, and

calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere;

(2) a process comprising the steps of:

supporting a ruthenium compound on a carrier,

calcining said supported one at a temperature of at

least 200°C in an atmosphere selected from the group

consisting of an oxidizing gas atmosphere, an inert gas

atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of hydrazine and an alkaline compound,

and

5 oxidizing said hydrazine-treated one wherein said supported ruthenium oxide catalyst has a carbon monoxide adsorption amount of at least 87.5 ml per one gram of ruthenium contained in the catalyst, which is measured by the following steps of:

10 reducing 0.1 g of said catalyst at 220°C for 60 minutes with flowing a hydrogen gas at a flow rate of 50 ml/min. under atmospheric pressure, and

conducting a metal surface area measuring method according to a carbon monoxide pulse;

15 (3) a process comprising the steps of:

supporting a ruthenium compound on a carrier,

calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas

20 atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of hydrazine and an alkaline compound,

and

oxidizing said hydrazine-treated one;

25 (4) a process comprising the steps of:

supporting a ruthenium compound on a carrier,  
and

calcining said supported one in an atmosphere selected  
from the group consisting of an oxidizing gas atmosphere,  
5 an inert gas atmosphere and a reducing gas atmosphere,  
wherein, when the peak intensity ratio of the produced  
catalyst and that of the catalyst after a 50 hours reaction  
test, which are measured by an extended X-ray absorption  
fine structure analysis (EXAFS) method, are A(b) and B(b)  
10 respectively, the peak intensity ratios A(b) and B(b)  
satisfy the following equation (1):

$$1 \leq B(b)/A(b) \leq 1.45 \quad (1)$$

provided that  $A(b) \leq 0.8$ ,

wherein A(b) is a peak intensity ratio of as-produced  
15 Catalyst b measured by the EXAFS method, and B(b) is a peak  
intensity ratio of Catalyst b measured by the EXAFS method  
after the 50 hours reaction test;  
in which

the 50 hours reaction test is carried out by filling  
20 supported ruthenium oxide Catalysts a and b in a reactor in  
this order from the inlet of the reactor in a weight ratio  
of 1:10 (Catalyst a to Catalyst b), and supplying, under  
atmospheric pressure, a hydrogen chloride gas at a flow  
rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an  
25 oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr.



to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at  $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , wherein Catalyst a is a catalyst having a chlorine formation activity per unit mass of catalyst of  $2 \times 10^{-4}$  to  $3 \times 10^{-4}$  mol/min.g-cat.,

5 which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at  $300^{\circ}\text{C}$  with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide Catalyst produced by the above process,

10 and in which

EXAFS method: Catalyst b is measured by an X-ray absorption fine structure analysis (XAFS) method at the Ru-K absorption edge, and the peak intensity of the catalyst is evaluated by the peak around 0.32 nm in a radial

15 distribution function obtained by the Fourier transformation of the EXAFS spectrum, wherein the peak intensity corresponds to the number of the second nearest neighbor ruthenium atoms of the X-ray absorbing ruthenium atoms in ruthenium dioxide, and the peak intensity ratio of the catalyst is calculated by dividing the peak intensity  
20 of the catalyst by that of ruthenium oxide having a particle size of at least 10 nm;

(5) a process comprising the following steps but not a treating step with hydrazine:

25 supporting a ruthenium compound on a titanium oxide

carrier containing the rutile crystal form,  
and

calcining said supported one at a temperature of 200°C  
to 600°C in an atmosphere selected from the group  
5 consisting of an oxidizing gas atmosphere, an inert gas  
atmosphere and a reducing gas atmosphere;  
and

(6) a process comprising the following steps but  
neither a calcining step nor a treating step with  
10 hydrazine:

supporting a ruthenium halide on a titanium oxide  
carrier containing the rutile crystal form,  
and

drying said supported one in an atmosphere selected  
15 from the group consisting of an oxidizing gas atmosphere,  
an inert gas atmosphere and a reducing gas atmosphere at a  
temperature of 20°C to less than 200°C.

5. The process according to claim 4, which is the  
process (2), (3) or (4), wherein said carrier is titanium  
20 oxide containing the rutile crystal form.

6. The process according to claim 4, which is the  
process (5), comprising the following steps but not a  
treating step with hydrazine:

supporting a ruthenium compound on a carrier,

25 and

calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, wherein the catalytic activity value of the produced catalyst and the catalytic activity value of the catalyst after 50 hours reaction test, which are measured by a catalytic activity test which is defined below, are respectively C(b) and D(b), and which satisfy the following equation (2):

$$0.79 \leq D(b)/C(b) \leq 1 \quad (2)$$

provided that  $C(b) \geq 3.0 \times 10^{-4}$  mol/min·g-cat

wherein C(b) is a catalytic activity value of the produced catalyst b, which is measured by the catalytic activity test and D(b) is a catalytic activity value of the catalyst b, which is measured by the catalytic activity test after a 50 hours reaction test;

in which

the 50 hours reaction test is carried out by filling supported ruthenium oxide Catalysts a and b in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and supplying, under atmospheric pressure, a hydrogen chloride gas at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr.

to carry out the reaction for 50 hours while maintaining

the hot spot of Catalyst b at  $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , wherein Catalyst a is a catalyst having a chlorine formation activity per unit mass of catalyst of  $2 \times 10^{-4}$  to  $3 \times 10^{-4}$  mol/min.g-cat., which is obtained in a reaction test for forming chlorine  
 5 by oxidizing hydrogen chloride with oxygen at  $300^{\circ}\text{C}$  with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide Catalyst produced by the above process, and in which

10 Catalytic activity test: 2.3 to 2.5 grams of a catalyst is diluted by mixing with 10 to 20 g of a spherical  $\alpha$ -alumina carrier having a diameter of 2 mm, and filled in a quartz reactor tube having an inner diameter of 12 mm, then a hydrogen chloride gas and an oxygen gas are  
 15 supplied in the reactor under atmospheric pressure at flow rates of 190 to 210 ml/min. and 190 to 210 ml/min., respectively (both volumes being converted to those at  $0^{\circ}\text{C}$  under 101 kPa) while heating the reactor in an electric furnace and maintaining the internal temperature (hot spot)  
 20 at  $300 \pm 1^{\circ}\text{C}$ , after  $2.0 \pm 1.0$  hours from the start of the reaction, an exit gas from the reactor is sampled by passing it through a 30 mass % aqueous solution of potassium iodide, the amount of formed chlorine and the  
 -----  
 amount of unreacted hydrogen chloride are measured by an  
 25 iodine titration method and a neutralization titration

method, respectively, and thereafter a chlorine formation activity per unit mass of the catalyst is calculated by the following equation and used as a catalyst activity:

$$\begin{aligned} &\text{Chlorine formation activity per unit mass of the catalyst} \\ &5 \quad (\text{mol/min.g-cat.}) = \\ &\quad \text{Amount of chlorine gas from reactor exit (mol/min.)} / \\ &\quad \text{catalyst weight (g)}. \end{aligned}$$

7. The process according to claim 4, which is the process (6), comprising the following steps but neither a calcining step nor a treating step with hydrazine:

supporting a ruthenium halide on a titanium oxide carrier containing the rutile crystal form, and

drying said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere at a temperature of 20°C to less than 200°C, wherein the catalytic activity value of the produced catalyst and the catalytic activity value of the catalyst after 50 hours reaction test, which are measured by a catalytic activity test which is defined below, are respectively E(b) and F(b), and which satisfy the following equation (3);

---


$$0.80 \leq F(b)/E(b) \leq 1.20 \quad (3)$$

provided that  $E(b) \geq 3.0 \times 10^{-4}$  mol/min.g-cat.,

in which

50 Hours reaction test: Supported ruthenium oxide Catalysts a and b are filled in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and a hydrogen chloride gas is supplied under atmospheric pressure at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at  $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , in which Catalyst a is a supported ruthenium oxide catalyst having a chlorine formation activity per unit mass of the catalyst of  $2 \times 10^{-4}$  to  $3 \times 10^{-4}$  mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at  $300^{\circ}\text{C}$  with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide catalyst produced by the above process, and in which

Catalytic activity test: 2.3 to 2.5 grams of a catalyst is diluted by mixing with 10 to 20 g of a spherical  $\alpha$ -alumina carrier having a diameter of 2 mm, and filled in a quartz reactor tube having an inner diameter of 12 mm, then a hydrogen chloride gas and an oxygen gas are supplied in the reactor under atmospheric pressure at flow rates of 190 to 210 ml/min. and 190 to 210 ml/min.

respectively (both volumes being converted to those at 0°C under 101 kPa) while heating the reactor in an electric furnace and maintaining the internal temperature (hot spot) at 300±1°C, after 2.0±1.0 hours from the start of the reaction, an exit gas from the reactor is sampled by passing it through a 30 mass % aqueous solution of potassium iodide, the amount of formed chlorine and the amount of unreacted hydrogen chloride are measured by an iodine titration method and a neutralization titration method, respectively, and thereafter a chlorine formation activity per unit mass of the catalyst is calculated by the following equation and used as a catalyst activity:

Chlorine formation activity per unit mass of the catalyst (mol/min.g-cat.) =

Amount of chlorine gas from reactor exit (mol/min.) / catalyst weight (g).

8. A process for producing chlorine by oxidizing hydrogen chloride with oxygen, which uses at least one catalyst selected from the group consisting of the following catalysts (1) to (6):

(1) a supported ruthenium oxide catalyst comprising titanium oxide which contains the rutile crystal form, and which is obtained by calcination at a temperature of at least 550°C, as a carrier;

(2) a supported ruthenium oxide catalyst having a

carbon monoxide adsorption amount of at least 87.5 ml per one gram of ruthenium contained in the catalyst, which is measured by the following steps of:

reducing 0.1 g of said catalyst at 220°C for 60  
5 minutes with flowing a hydrogen gas at a flow rate of 50 ml/min. under atmospheric pressure, and

conducting a metal surface area measuring method according to a carbon monoxide pulse;

(3) a supported ruthenium oxide catalyst obtained by a  
10 preparation process comprising the steps of:

supporting a ruthenium compound on a carrier,

calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas  
15 atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of hydrazine and an alkaline compound,  
and

oxidizing said hydrazine-treated one;

(4) a supported ruthenium oxide catalyst produced by a  
20 process comprising the steps of:

supporting a ruthenium compound on a carrier,

and

calcining said supported one in an atmosphere selected  
25 from the group consisting of an oxidizing gas atmosphere,



an inert gas atmosphere and a reducing gas atmosphere,  
wherein, when the peak intensity ratio of the produced  
catalyst and that of the catalyst after a 50 hours reaction  
test, which are measured by an extended X-ray absorption  
5 fine structure analysis (EXAFS) method, are A(b) and B(b)  
respectively, the peak intensity ratios A(b) and B(b)  
satisfy the following equation (1):

$$1 \leq B(b)/A(b) \leq 1.45 \quad (1)$$

provided that  $A(b) \leq 0.8$ ,

10 wherein A(b) is a peak intensity ratio of as-produced  
Catalyst b measured by the EXAFS method, and B(b) is a peak  
intensity ratio of Catalyst b measured by the EXAFS method  
after the 50 hours reaction test;  
in which

15 50 Hours reaction test: Supported ruthenium oxide  
Catalysts a and b are filled in a reactor in this order  
from the inlet of the reactor in a weight ratio of 1:10  
(Catalyst a to Catalyst b), and a hydrogen chloride gas is  
supplied under atmospheric pressure at a flow rate of 0.185  
20 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a  
flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the  
reaction for 50 hours while maintaining the hot spot of  
Catalyst b at  $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , in which Catalyst a is a supported  
ruthenium oxide catalyst having a chlorine formation  
25 activity per unit mass of the catalyst of  $2 \times 10^{-4}$  to  $3 \times$

10<sup>-4</sup> mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at 300°C with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium  
5 oxide catalyst produced by the above process, and in which

EXAFS method: Catalyst b is measured by an X-ray absorption fine structure analysis (XAFS) method at the Ru-K absorption edge, and the peak intensity of the catalyst  
10 is evaluated by the peak around 0.32 nm in a radial distribution function obtained by the Fourier transformation of the EXAFS spectrum, wherein the peak intensity corresponds to the number of the second nearest neighbor ruthenium atoms of the X-ray absorbing ruthenium  
15 atoms in ruthenium dioxide, and the peak intensity ratio of the catalyst is calculated by dividing the peak intensity of the catalyst by that of ruthenium oxide having a particle size of at least 10 nm;

(5) a supported ruthenium oxide catalyst produced by a  
20 process comprising the following steps but not a treating step with hydrazine:

supporting a ruthenium compound on a titanium oxide carrier containing the rutile form,

---

and

25 calcining said supported one at a temperature of 200°C

to 600°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere;  
and

5 (6) a supported ruthenium oxide catalyst produced by a process comprising the following steps but neither a calcining step nor a treating step with hydrazine:

supporting a ruthenium halide on a titanium oxide carrier containing the rutile crystal form,

10 and

drying said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere at a temperature of 20°C to less than 200°C.

15 9. The process according to claim 8, wherein said catalyst (2) is prepared by the process described in (3).

10. The process according to claim 8, wherein said catalyst is any one of the supported ruthenium oxide catalysts (2), (3) and (4) comprising titanium oxide  
20 containing the rutile crystal form as a carrier.

11. The process according to claim 8, wherein said catalyst is the supported ruthenium oxide catalyst (5), wherein the catalyst is produced by a process comprising  
the following steps but not a treating step with hydrazine:

25 supporting a ruthenium compound on a carrier,

and

calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, wherein the catalytic activity value of the produced catalyst and the catalytic activity value of the catalyst after 50 hours reaction test, which are measured by a catalytic activity test which is defined below, are respectively C(b) and D(b), and which satisfy the following equation (2):

$$0.79 \leq D(b)/C(b) \leq 1 \quad (2)$$

provided that  $C(b) \geq 3.0 \times 10^{-4}$  mol/min.g-cat.

wherein C(b) is a catalytic activity value of the produced catalyst b, which is measured by the catalytic activity test and D(b) is a catalytic activity value of the catalyst b, which is measured by the catalytic activity test after a 50 hours reaction test; in which

the 50 hours reaction test is carried out by filling supported ruthenium oxide Catalysts a and b in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and supplying, under atmospheric pressure, a hydrogen chloride gas at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr.





equation (3):

$$0.80 \leq F(b)/E(b) \leq 1.20 \quad (3)$$

provided that  $E(b) \geq 3.0 \times 10^{-4}$  mol/min.g-cat.

in which

5           50 Hours reaction test: Supported ruthenium oxide  
Catalysts a and b are filled in a reactor in this order  
from the inlet of the reactor in a weight ratio of 1:10  
(Catalyst a to Catalyst b), and a hydrogen chloride gas is  
supplied under atmospheric pressure at a flow rate of 0.185  
10 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a  
flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the  
reaction for 50 hours while maintaining the hot spot of  
Catalyst b at  $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , in which Catalyst a is a supported  
ruthenium oxide catalyst having a chlorine formation  
15 activity per unit mass of the catalyst of  $2 \times 10^{-4}$  to  $3 \times$   
 $10^{-4}$  mol/min.g-cat., which is obtained in a reaction test  
for forming chlorine by oxidizing hydrogen chloride with  
oxygen at  $300^{\circ}\text{C}$  with a molar ratio of hydrogen chloride to  
oxygen being 1:1, and Catalyst b is a supported ruthenium  
20 oxide catalyst produced by the above process,  
and in which

Catalytic activity test: 2.3 to 2.5 grams of a  
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spherical  $\alpha$ -alumina carrier having a diameter of 2 mm, and  
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(54) Title: **SUPPORTED RUTHENIUM OXIDE CATALYST, PROCESS FOR PREPARING SUPPORTED RUTHENIUM CATALYST AND PROCESS FOR PRODUCING CHLORINE**

(57) Abstract: A supported ruthenium oxide catalyst selected from the group consisting of (1) a supported ruthenium oxide catalyst comprising TiO<sub>2</sub> which contains the rutile crystal form, and which is obtained by calcination at a temperature of at least 550 °C, as a carrier; (2) a supported ruthenium oxide catalyst having a carbon monoxide adsorption amount of at least 87.5 ml per one gram of ruthenium contained in the catalyst; (3) a supported ruthenium oxide catalyst obtained by a preparation process comprising the steps of supporting a ruthenium compound on a carrier, calcining the supported one at a temperature of at least 200 °C in an oxidizing gas atmosphere, an inert gas atmosphere or a reducing gas atmosphere, treating the calcined one with a mixed solution of hydrazine and an alkaline compound, and oxidizing the hydrazine-treated one. These catalysts have a high catalytic activity and thus produce chlorine in a smaller amount at a lower temperature.

WO 01/10550 A1

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0020-4951P

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<u>222292/1999</u>	<u>Japan</u>	<u>8/5/1999</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
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inventor, if any:  
see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Residence (City, State & Country)		CITIZENSHIP
MAILING ADDRESS (Complete Street Address including City, State & Country)		

Name of Tenth  
inventor, if any:  
see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Residence (City, State & Country)		CITIZENSHIP
MAILING ADDRESS (Complete Street Address including City, State & Country)		

Name of Eleventh  
inventor, if any:  
see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Residence (City, State & Country)		CITIZENSHIP
MAILING ADDRESS (Complete Street Address including City, State & Country)		

Name of Twelfth  
inventor, if any:  
see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Residence (City, State & Country)		CITIZENSHIP
MAILING ADDRESS (Complete Street Address including City, State & Country)		